Supporting Information

Metal-free nitro/azido cyclization of 1-acryloyl-2-cyanoindoles to access NO_2/N_3-featured pyrrolo[1,2-a] indolediones

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General Information

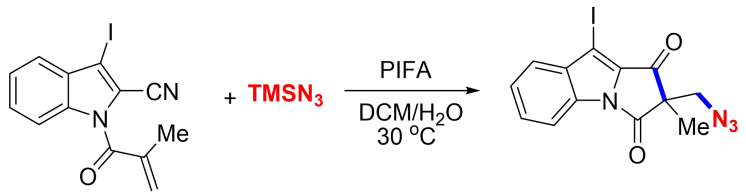
^{1}H and ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker advance III 400 or 600 spectrometer in $CDCl_3$ with TMS as the internal standard. High-resolution mass spectral analysis (HRMS) data were measured on a Waters Xevo G2-XS qTOF. All products were identified by ^{1}H and ^{13}C NMR, HRMS. The raw materials were purchased from Energy, Meryer, J&K Chemicals, or Aldrich and used without further purification.

Typical procedure for the reaction

Reaction conditions 1: A mixture of 1-acryloyl-2-cyanoindoles (1 equiv., 0.1 mmol), TBN (3 equiv., 0.3 mmol), EA (3 mL), and H_2O (0.5 mL) was added into a 15 mL sealed pipe, which was conducted at 100 °C in a heating mantle with an air atmosphere. After the nitro cyclization process was finished in 12 hours, the mixture was condensed under vacuum and purified by column chromatography to afford the corresponding nitro products.

Reaction conditions 2: A mixture of 1-acryloyl-2-cyanoindoles (1 equiv., 0.1 mmol), $TMSN_3$ (2 equiv., 0.2 mmol), PIFA (4 equiv., 0.4 mmol), dichloromethane (DCM, 2 mL), and H_2O (1 mL) was added into a 15 mL sealed pipe, which was conducted at 30 °C in an oil bath with an air atmosphere. After the transformation was completed in 12 hours, a similar workup was operated.

Table S1 Reaction condition optimization[a]



Entry	N_3 source (equiv.)	Oxidant (equiv.)	Solvent (mL)	Temp. (^{O}C)	Time (h)	Yield[b] (%)
1	$TMSN_3$ (2)	PIFA (2)	DCM: H_2O (2:0.5)	30	12	45
2	$TMSN_3$ (2.5)	PIFA (2)	DCM: H_2O	30	12	45

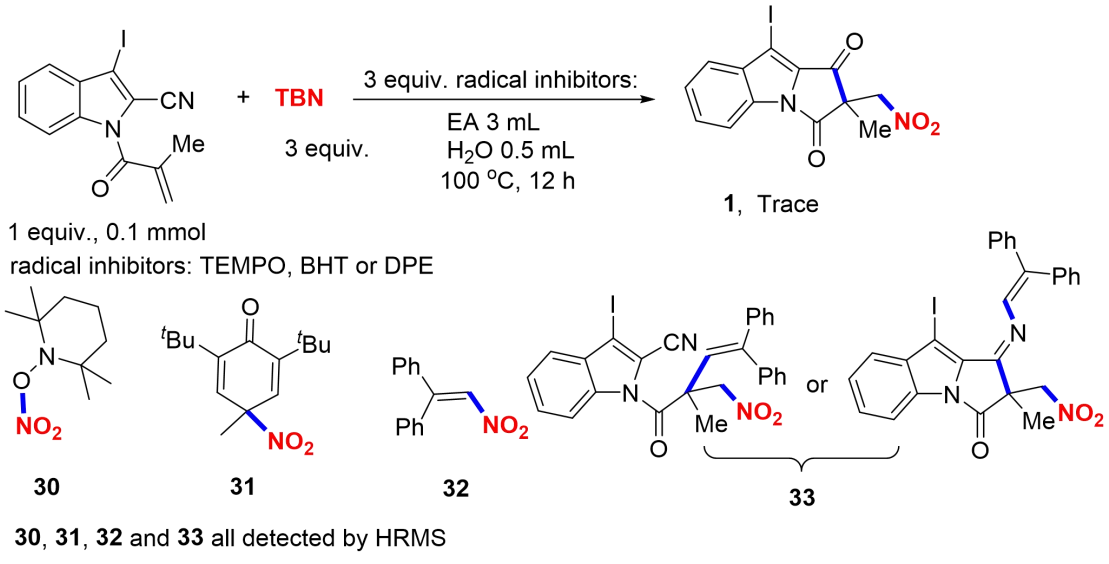
			(2:0.5)			
3	$TMSN_3$ (3)	PIFA (2)	DCM: H_2O (2:0.5)	30	12	47
4	NaN_3 (2)	PIFA (2)	DCM: H_2O (2:0.5)	30	12	37
5	$TMSN_3$ (2)	PIFA (2)	DCM: H_2O (2:0.5)	50	12	40
6	$TMSN_3$ (2)	PIFA (2)	DCM: H_2O (2:0.5)	80	12	34
7	$TMSN_3$ (2)	DIB (2)	DCM: H_2O (2:0.5)	30	12	NR
8	$TMSN_3$ (2)	I_2O_5 (2)	DCM: H_2O (2:0.5)	30	12	NR
9	$TMSN_3$ (2)	PIFA (3)	DCM: H_2O (2:0.5)	30	12	50
10	$TMSN_3$ (2)	PIFA (4)	DCM: H_2O (2:0.5)	30	12	56
11	$TMSN_3$ (2)	PIFA (4)	DCM: H_2O (1:0.5)	30	12	51
12	$TMSN_3$ (2)	PIFA (4)	DCM: H_2O (3:0.5)	30	12	50
13	$TMSN_3$ (2)	PIFA (4)	DCM: H_2O (2:1.5)	30	12	48
14	**$TMSN_3$ (2)**	**PIFA (4)**	**DCM: H_2O (2:1)**	**30**	**12**	**61**
15	$TMSN_3$ (2)	PIFA (4)	DCE: H_2O (2:1)	30	12	36
16	$TMSN_3$ (2)	PIFA (4)	CH_3CN: H_2O (2:1)	30	12	46

17	$TMSN_3$ (2)	PIFA (4)	DMF: H_2O (2:1)	30	12	27
18	$TMSN_3$ (2)	PIFA (4)	EA: H_2O (2:1)	30	12	44

[a]Reaction conditions: 1-acryloyl-2-cyanoindoles (1 equiv., 0.1 mmol), $TMSN_3$ (2 equiv.), PIFA (4 equiv.), dichloromethane (DCM, 2 mL), H_2O (1 mL), 30 °C, air, 12 h. [b]Isolated yields.

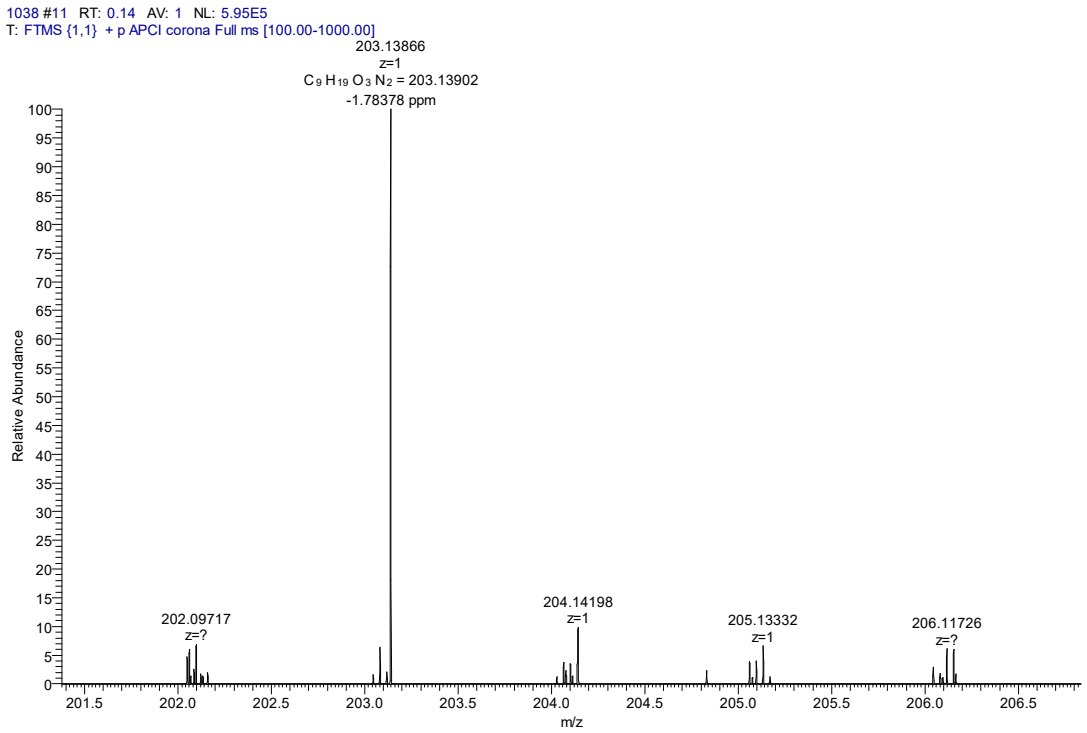
The detailed reaction condition optimization of the azide cyclization process was described as shown in Table S1. First, The variation of the azide sources and hypervalent iodines indicated that 2 equiv. $TMSN_3$/4 equiv. PIFA was best for this cascade system (entries 1-10). Next, after adjusting the kinds and volume of the co-solvents, we found that 2 mL DCM and 1 mL H_2O were the optimal co-solvents (entries 11-18). Finally, the optimum reaction system was listed as follows: 1-acryloyl-2-cyanoindoles (1 equiv., 0.1 mmol), $TMSN_3$ (2 equiv.), PIFA (4 equiv.), dichloromethane (DCM, 2 mL), H_2O (1 mL), 30 °C, air, 12 h.

Mechanistic studies

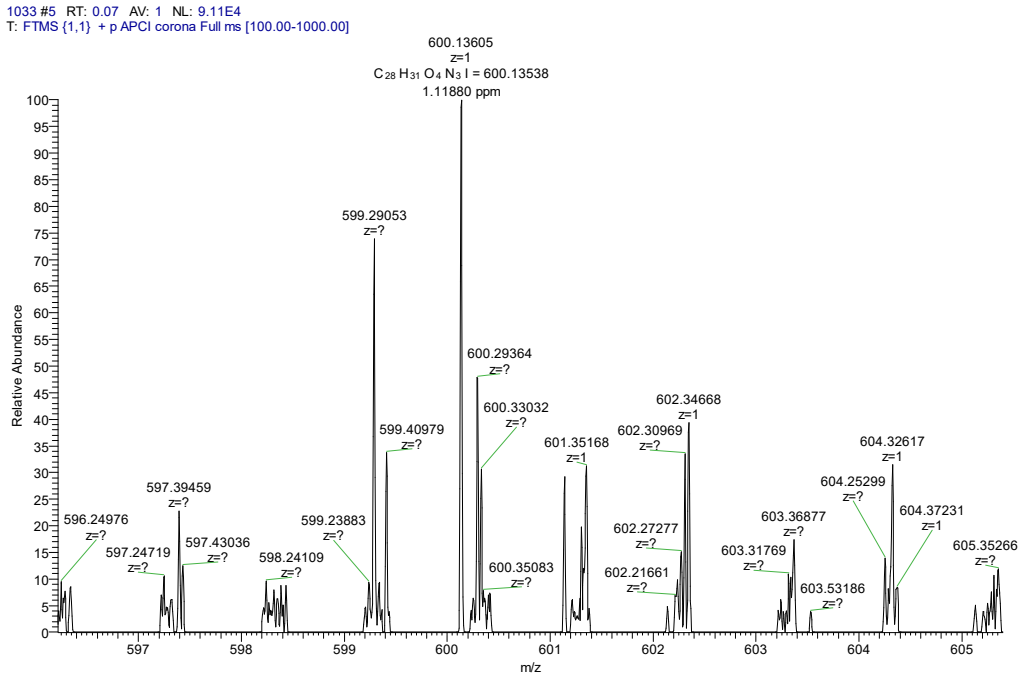


30, **31**, **32** and **33** all detected by HRMS

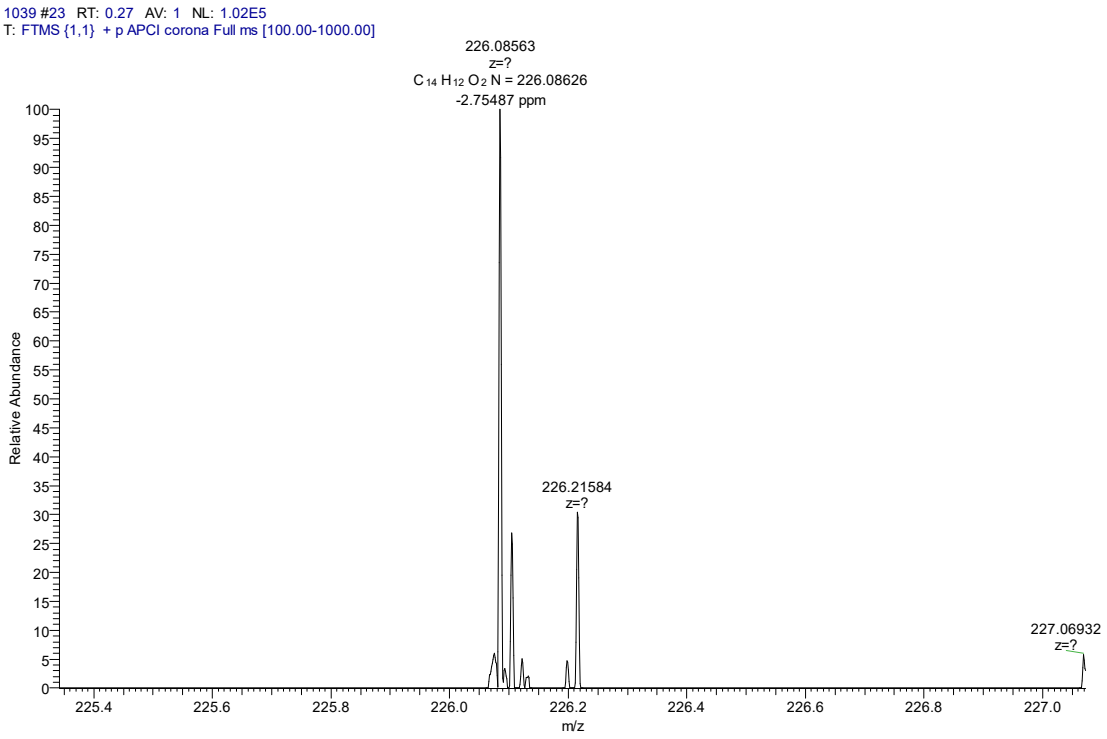
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
30	$C_9H_{18}N_2O_3$	$C_9H_{19}N_2O_3$	203.1389	203.1390	-0.05



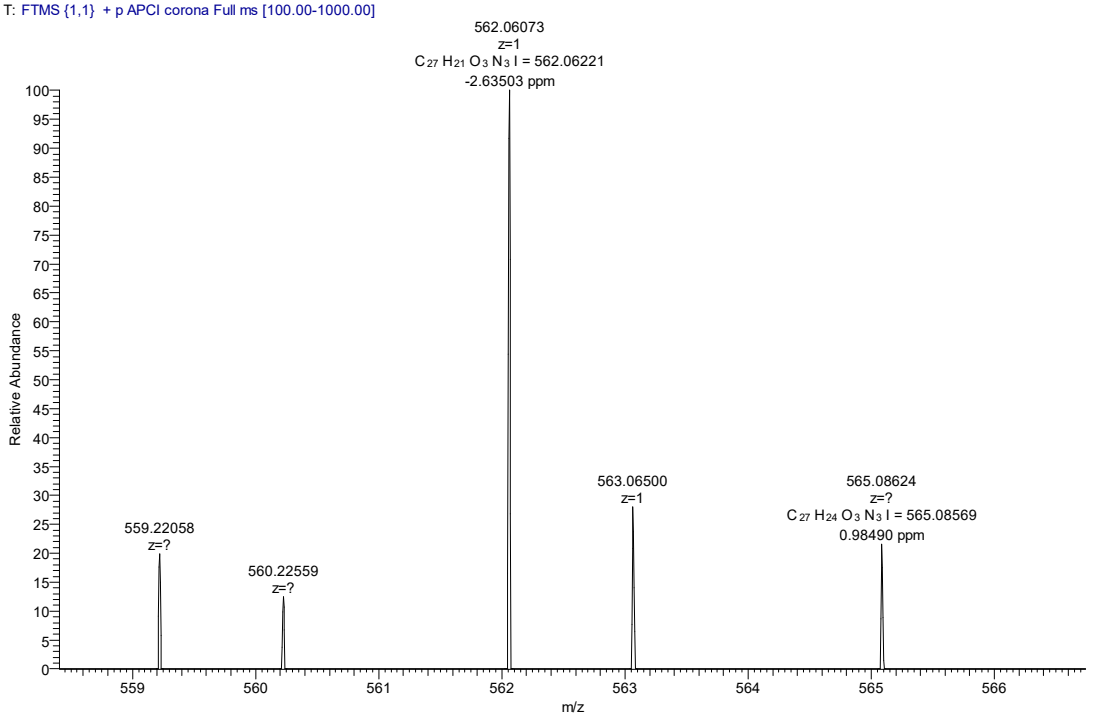
Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
31	$C_{28}H_{32}IN_3O_4$	$C_{28}H_{31}IN_3O_4$	600.1361	600.1354	0.12



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
32	$C_{14}H_{11}NO_2$	$C_{14}H_{12}NO_2$	226.0856	226.0863	-0.31



Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
33	$C_{27}H_{20}IN_3O_3$	$C_{27}H_{21}IN_3O_3$	562.0607	562.0622	-0.27



Crystallographic details

(1) First, nitro product **6** was solved with the mixture of 1.5 mL acetonitrile and 3 mL diethyl ether in a sample bottle, respectively, which was sealed/placed on the desk of the laboratory. Next, the crystal of the fused cycle **6** was precipitated via volatilizing after several days.

(2) A single crystal of product **6** was obtained as follows: A proper crystal was selected and detected on a "Bruker APEX2" diffractometer. The crystal stayed at 299.0 K during data collection. With the assistance of Shelxtl, the structure was solved with the XShell structure solution program using Charge Flipping, and it was refined with the SHELXL [1] refinement package using Least Squares minimisation. Finally, crystal data and structure refinement parameters of product 6 are described as shown in **Table S1**. CCDC No. 2361719.

[1]. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table S1. Crystal data and structure refinement for product **6.**

CCDC	2361719
Displacement ellipsoids are drawn at the 30% probability level	
Empirical formula	$C_{19}H_{13}ClN_2O_4$
Formula weight	368.779
Temperature/K	299.00
Crystal system	triclinic
Space group	P-1
a/Å	10.670(9)
b/Å	10.941(10)
c/Å	28.681(19)
α/°	89.79(3)
β/°	89.93(3)
γ/°	89.86(3)
Volume/Å^3	3348(5)

Z	8
ρ_{calc}g/cm^3	1.463
μ/mm^{-1}	0.257
F(000)	1522.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.82 to 42.64
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -29 ≤ l ≤ 29
Reflections collected	23978
Independent reflections	7374 [R_{int} = 0.0722, R_{sigma} = 0.0748]
Data/restraints/parameters	7374/0/941
Goodness-of-fit on F^2	1.127
Final R indexes [I>=2σ (I)]	R_1 = 0.0556, wR_2 = 0.1088
Final R indexes [all data]	R_1 = 0.1044, wR_2 = 0.1370
Largest diff. peak/hole / e Å^{-3}	0.39/-0.54

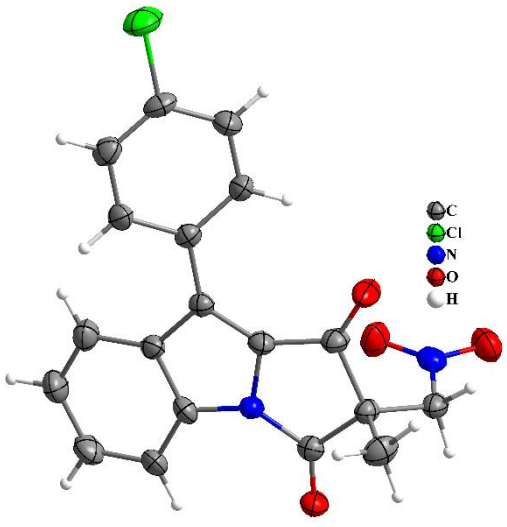
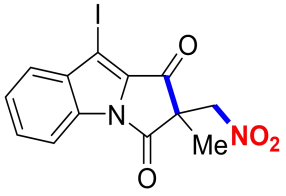


Fig. S1 Structure of product **6**.

Physical data for the following products:

1. 9-iodo-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

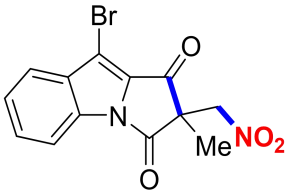
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 35.4 mg, yield 92 %.



^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 4.99 (d, *J* = 16.2 Hz, 1H), 4.95 (d, *J* = 16.2 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 187.0, 167.3, 136.7, 135.5, 132.6, 130.1, 126.2, 124.4, 115.3, 74.9, 68.7, 55.2, 18.5. HRMS (ESI, m/z): Calculated for $C_{13}H_{10}N_2O_4I$ $(M+H)^+$ 384.9680, found 384.9676.

2. 9-bromo-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

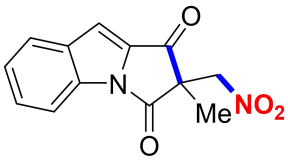
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 30.4 mg, yield 90 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 4.99 (d, *J* = 16.4 Hz, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 167.4, 133.6, 132.2, 131.6, 130.2, 126.2, 122.6, 115.4, 100.6, 74.9, 55.2, 18.6. HRMS (ESI, m/z): Calculated for $C_{13}H_9N_2O_4BrNa$ $(M+Na)^+$ 358.9638, found 358.9637.

3. 2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

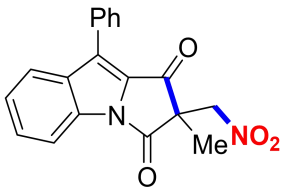
A yellow oily liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 16 mg, yield 62 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, J = 8.4, 0.8 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.47 – 7.43 (m, 1H), 7.31 (s, 1H), 4.96 (s, 2H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 168.1, 134.8, 133.7, 132.9, 129.1, 125.7, 124.4, 115.3, 108.9, 74.9, 55.0, 18.6. HRMS (ESI, m/z): Calculated for $C_{13}H_{10}N_2O_4Na$ $(M+Na)^+$ 281.0533, found 281.0533.

4. 2-methyl-2-(nitromethyl)-9-phenyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

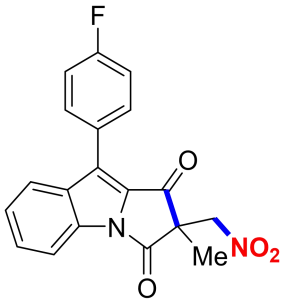
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 26.7 mg, yield 80 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.2 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 4.97 (s, 2H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.2, 133.1, 132.7, 130.2, 129.7, 129.5, 129.4, 128.9, 126.6, 125.9, 123.7, 115.6, 75.0, 55.3, 18.8. HRMS (ESI, m/z): Calculated for $C_{19}H_{14}N_2O_4Na$ $(M+Na)^+$ 357.0846, found 357.0844.

5. 9-(4-fluorophenyl)-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 32 mg, yield 91 %. Mp: 89-90 °C.

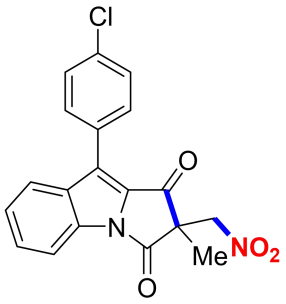


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.92 (dd, J = 8.4, 5.6 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.50 (dd, J = 8.0, 7.6 Hz, 1H), 7.27 – 7.23 (m, 2H), 4.97 (s, 2H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 168.1, 163.3(d, J = 248.9 Hz), 132.8(d, J = 45.6 Hz), 131.5, 131.4, 129.6, 129.5,

126.3(d, J = 3.3 Hz), 125.9, 125.4, 123.4, 116.1, 115.9, 115.6, 75.0, 55.3, 18.7. ^{19}F NMR (565 MHz, $CDCl_3$): δ -110.69 (s, 1F). HRMS (ESI, m/z): Calculated for $C_{19}H_{13}FN_2O_4Na$ $(M+Na)^+$ 375.0752, found 375.0752.

6. 9-(4-chlorophenyl)-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

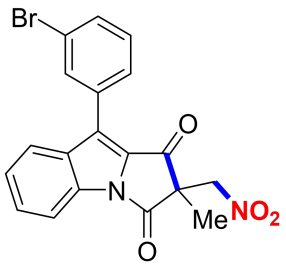
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 30.2 mg, yield 82 %. Mp: 126-127 °C.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.88 – 7.86 (m, 2H), 7.70 – 7.64 (m, 1H), 7.55 – 7.48 (m, 3H), 4.98 (s, 2H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 168.1, 135.5, 133.0, 132.4, 130.7, 129.9, 129.8, 129.5, 129.3, 129.2, 128.6, 126.0, 125.1, 123.3, 115.6, 75.0, 55.2, 18.7. HRMS (ESI, m/z): Calculated for $C_{19}H_{13}ClN_2O_4Na$ $(M+Na)^+$ 391.0456, found 391.0456.

7. 9-(3-bromophenyl)-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 30.2 mg, yield 73 %.

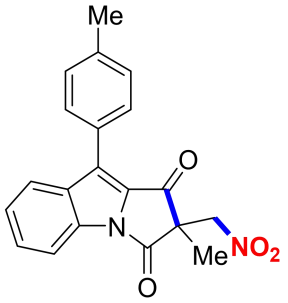


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 8.07 (t, J = 2.0 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.70 – 7.66 (m, 1H), 7.63-7.61 (m, 1H), 7.54 – 7.49 (m, 1H), 7.43 (t, J = 8.0 Hz, 1H), 4.98 (s, 2H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.1, 132.9, 132.3, 132.2, 132.1, 130.4, 130.0, 129.6, 128.1,

126.1, 124.5, 123.3, 122.9, 115.6, 75.0, 55.2, 18.7. HRMS (ESI, m/z): Calculated for $C_{19}H_{13}BrN_2O_4Na$ $(M+Na)^+$ 436.9933, found 436.9929.

8. 2-methyl-2-(nitromethyl)-9-(p-tolyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

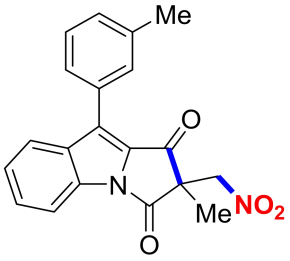
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 29.3 mg, yield 86 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.61 (m, 1H), 7.50 – 7.46 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.97 (s, 2H), 2.45 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.2, 139.8, 133.1, 132.8, 129.8, 129.6, 129.5, 129.4, 129.3, 128.6, 127.3, 126.8, 125.8, 123.7, 115.5, 75.0, 55.2, 21.5, 18.8. HRMS (ESI, m/z): Calculated for $C_{20}H_{16}N_2O_4Na$ $(M+Na)^+$ 371.1002, found 371.1001.

9. 2-methyl-2-(nitromethyl)-9-(m-tolyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 28.5 mg, yield 82 %. Mp: 144-145 °C.

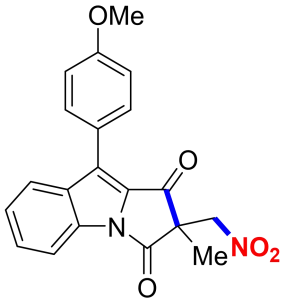


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.46 (dt, *J* = 15.6, 7.6 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 4.96 (s, 2H), 2.48 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.2, 138.6, 133.0, 132.8, 130.3, 130.1, 129.7, 129.3, 128.8, 126.8, 126.6,

125.8, 123.78, 115.5, 75.0, 55.3, 21.5, 18.8. HRMS (ESI, m/z): Calculated for $C_{20}H_{16}N_2O_4Na$ $(M+Na)^+$ 371.1002, found 371.1001.

10. 9-(4-methoxyphenyl)-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

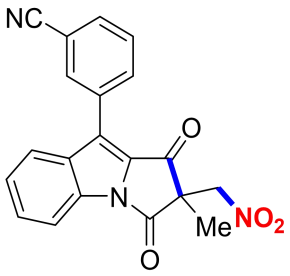
A green solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 30.2 mg, yield 83 %. Mp: 122-123 °C.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 3.90 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.1, 160.6, 133.1, 132.8, 131.0, 129.3, 129.1, 126.7, 125.7, 123.7, 122.7, 115.5, 114.4, 75.0, 55.4, 55.3, 18.8. HRMS (ESI, m/z): Calculated for $C_{20}H_{16}N_2O_5Na$ $(M+Na)^+$ 387.0951, found 387.0950.

11. 3-(2-methyl-2-(nitromethyl)-1,3-dioxo-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)benzonitrile

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), 26.9 mg, yield 75 %. Mp: 142-143 °C.

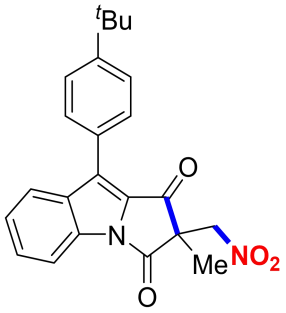


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 1.2 Hz, 1H), 8.19 – 8.16 (m, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.79-7.61 (m, 1H), 7.72 (dd, *J* = 9.8, 2.2 Hz, 1H), 7.68 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.56 – 7.52 (m, 1H), 4.99 (s, 2H), 1.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 168.1, 133.7, 132.9, 132.7, 132.6, 132.0, 131.7, 130.3, 129.8, 129.7, 126.4, 123.3, 122.8, 118.3, 115.8, 113.3, 75.00, 55.2, 18.7.

HRMS (ESI, m/z): Calculated for $C_{20}H_{13}N_3O_4Na$ $(M+Na)^+$ 382.0798, found 382.0797.

12. 9-(4-(tert-butyl)phenyl)-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

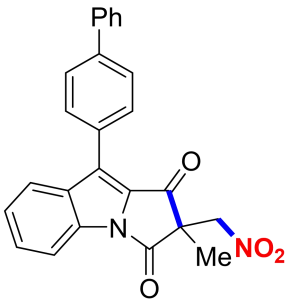
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), 35.1 mg, yield 90 %. Mp: 124-125 °C.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 4.97 (s, 2H), 1.53 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.16, 152.8, 133.1, 132.8, 129.5, 129.3, 129.2, 127.3, 126.7, 125.9, 125.7, 123.8, 115.5, 75.0, 55.3, 34.9, 31.2, 18.8. HRMS (ESI, m/z): Calculated for $C_{23}H_{22}N_2O_4Na$ $(M+Na)^+$ 413.1472, found 413.1470.

13. 9-([1,1'-biphenyl]-4-yl)-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 31.2 mg, yield 76 %. Mp: 151-152 °C.

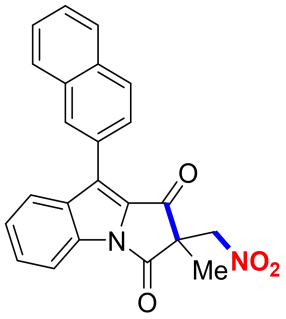


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.68 (dd, *J* = 7.2, 5.6 Hz, 3H), 7.50 (dd, *J* = 16.4, 8.4 Hz, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 4.98 (s, 2H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 168.2, 142.3, 140.3, 133.1, 132.7, 129.9, 129.7, 129.4,

129.2, 128.9, 127.8, 127.6, 127.1, 126.2, 125.9, 123.7, 115.6, 75.0, 55.3, 18.8. HRMS (ESI, m/z): Calculated for $C_{25}H_{18}N_2O_4Na$ $(M+Na)^+$ 433.1159, found 433.1158.

14. 2-methyl-9-(naphthalen-2-yl)-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

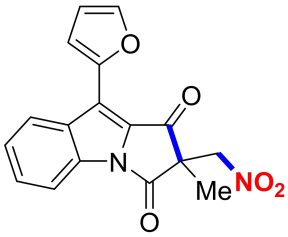
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 29.2 mg, yield 76 %. Mp: 102-103 °C.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.06 (s, 2H), 8.04 – 8.00 (m, 1H), 7.97 – 7.95 (m, 1H), 7.74 (t, J = 7.2 Hz, 1H), 7.62 – 7.55 (m, 3H), 5.03 (s, 2H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.2, 133.6, 133.3, 133.1, 132.9, 129.9, 129.5, 129.2, 128.6, 128.5, 127.8, 127.7, 127.1, 126.8, 126.6, 126.0, 123.7, 115.6, 75.0, 55.3, 18.8. HRMS (ESI, m/z): Calculated for $C_{23}H_{16}N_2O_4Na$ $(M+Na)^+$ 407.1002, found 407.1002.

15. 9-(furan-2-yl)-2-methyl-2-(nitromethyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

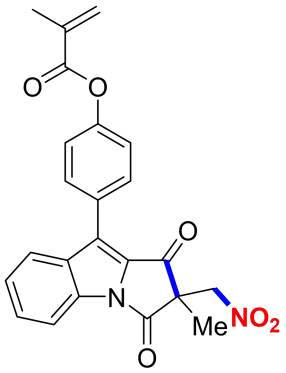
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 17.0 mg, yield 52 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 3.2 Hz, 1H), 7.67 (dd, J = 12.8, 4.8 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 6.65 (s, 1H), 5.00 (d, J = 16.0 Hz, 1H), 4.95 (d, J = 16.0 Hz, 1H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 168.1, 147.9, 144.2, 133.0, 130.7, 129.7, 127.4, 126.0, 125.7, 115.6, 115.2, 114.4, 112.5, 75.0, 55.2, 18.9. HRMS (ESI, m/z): Calculated for $C_{17}H_{12}N_2O_5Na$ $(M+Na)^+$ 347.0638, found 347.0638.

16. 4-(2-methyl-2-(nitromethyl)-1,3-dioxo-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)phenyl methacrylate

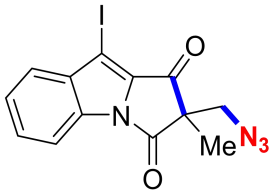
A green liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 17.1 mg, yield 41 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 5.81 (d, *J* = 1.3 Hz, 1H), 4.97 (s, 2H), 2.10 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 168.2, 165.6, 151.7, 135.7, 133.0, 132.6, 130.7, 129.5, 127.8, 127.7, 126.0, 125.6, 123.5, 122.2, 115.6, 75.0, 55.3, 18.8, 18.4. HRMS (ESI, m/z): Calculated for $C_{23}H_{18}N_2O_6Na$ $(M+Na)^+$ 441.1057, found 441.1055.

17. 2-(azidomethyl)-9-iodo-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 23.2 mg, yield 61 %.

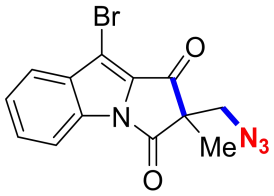


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 – 8.16 (m, 1H), 7.67-7.64 (m, 2H), 7.52 – 7.49 (m, 1H), 3.90 (d, *J* = 12.0 Hz, 1H), 3.86 (d, *J* = 12.0 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 189.6, 168.8, 137.0, 136.0, 132.4, 129.9, 127.3, 126.2, 124.4,

115.5, 67.2, 57.6, 54.5, 17.4. HRMS (ESI, m/z): Calculated for $C_{13}H_{10}N_4O_2I$ $(M+H)^+$ 380.9843, found 380.9837.

18. 2-(azidomethyl)-9-bromo-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

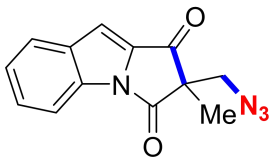
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 16.7 mg, yield 50 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 3.90 (d, J = 12.0 Hz, 1H), 3.86 (d, J = 12.0 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 169.0, 133.8, 132.1, 131.9, 130.0, 126.1, 122.6, 115.5, 99.2, 57.6, 54.5, 17.4. HRMS (ESI, m/z): Calculated for $C_{13}H_9BrN_4O_2Na$ $(M+Na)^+$ 354.9801, found 354.9801.

19. 2-(azidomethyl)-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

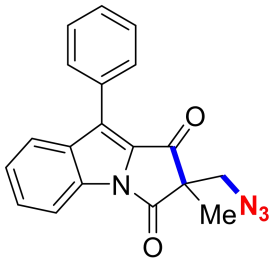
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 10.4 mg, yield 41 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.25 (s, 1H), 3.87 (s, 2H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 169.7, 135.4, 134.0, 132.6, 128.9, 125.7, 124.3, 115.5, 107.7, 57.3, 54.5, 17.5. HRMS (ESI, m/z): Calculated for $C_{13}H_{10}N_4O_2Na$ $(M+Na)^+$277.0696, found 277.0697.

20. 2-(azidomethyl)-2-methyl-9-phenyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

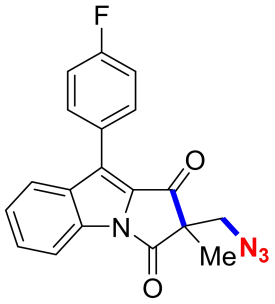
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 20.1 mg, yield 62 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.51 – 7.46 (m, 2H), 3.91 (d, *J* = 11.6 Hz, 1H), 3.87 (d, *J* = 11.6 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 169.7, 133.0, 132.7, 130.3, 130.2, 129.5, 129.3, 129.2, 128.9, 125.8, 125.3, 123.6, 115.7, 57.6, 54.6, 17.7. HRMS (ESI, m/z): Calculated for $C_{19}H_{14}N_4O_2Na$ $(M+Na)^+$ 353.1009, found 353.1009.

21. 2-(azidomethyl)-9-(4-fluorophenyl)-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

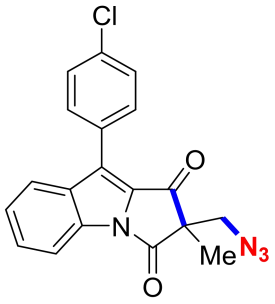
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 15.3 mg, yield 44 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.69 – 7.65 (m, 1H), 7.48 (dd, *J* = 14.8, 7.2 Hz, 1H), 7.27-7.23 (m, 2H), 3.90 (d, *J* = 12.0 Hz, 1H), 3.87 (d, *J* = 12.0 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 169.6, 163.2(d, *J* = 248.6 Hz), 132.7(d, *J* = 7.8 Hz), 131.4(d, *J* = 8.3 Hz), 130.2, 129.3, 126.4, 125.9, 124.2, 123.3, 116.1, 115.9, 115.7, 57.6, 54.6, 17.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -110.94(s, 1F). HRMS (ESI, m/z): Calculated for $C_{19}H_{14}FN_4O_2$ $(M+H)^+$ 349.1095, found 349.1087.

22. 2-(azidomethyl)-9-(4-chlorophenyl)-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

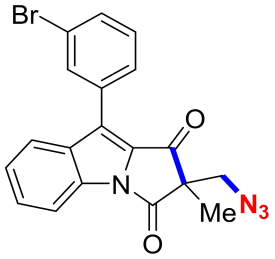
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 16.4 mg, yield 45 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.54-7.49 (m, 3H), 3.91 (d, *J* = 12.0 Hz, 1H), 3.87 (d, *J* = 12.0 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 169.6, 135.3, 132.7, 130.7, 129.5, 129.4, 129.1, 128.8, 126.9, 126.0, 123.9, 123.3, 115.8, 57.6, 54.6, 17.6. HRMS (ESI, m/z): Calculated for $C_{19}H_{13}ClN_4O_2Na$ $(M+Na)^+$ 387.0619, found 387.0619.

23. 2-(azidomethyl)-9-(3-bromophenyl)-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

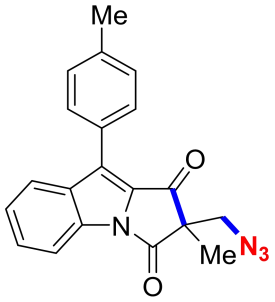
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 19.2 mg, yield 47%.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.0 Hz, 1H), 8.08 (t, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.70 – 7.66 (m, 1H), 7.63-7.60 (m, 1H), 7.53 – 7.48 (m, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 12.0 Hz, 1H), 3.88 (d, *J* = 9.2 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 169.7, 132.6, 132.5, 132.4, 132.2, 132.1, 130.6, 130.4, 129.4, 128.1, 126.1, 123.3, 123.2, 122.8, 115.7, 57.6, 54.6, 17.6. HRMS (ESI, m/z): Calculated for $C_{19}H_{13}BrN_4O_2Na$ $(M+Na)^+$ 433.0096, found 433.0094.

24. 2-(azidomethyl)-2-methyl-9-(p-tolyl)-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

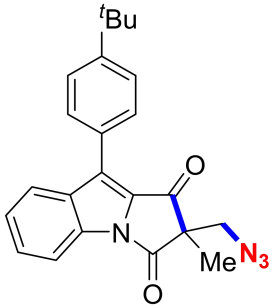
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 22.0 mg, yield 64 %. Mp: 120-121 °C.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.49 – 7.45 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.90 (d, *J* = 12.0 Hz, 1H), 3.86 (d, *J* = 11.6 Hz, 1H), 2.46 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 169.7, 139.6, 133.0, 132.8, 130.1, 129.6, 129.4, 129.1, 127.4, 125.7, 125.6, 123.7, 115.6, 57.6, 54.6, 21.5, 17.7. HRMS (ESI, m/z): Calculated for $C_{20}H_{16}N_4O_2Na$ $(M+Na)^+$ 367.1165, found 367.1166.

25. 2-(azidomethyl)-9-(4-(tert-butyl)phenyl)-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

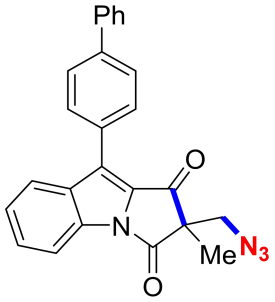
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 22.0 mg, yield 57 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.59 – 7.57 (m, 2H), 7.49 – 7.45 (m, 1H), 3.90 (d, *J* = 12.0 Hz, 1H), 3.86 (d, *J* = 12.0 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 169.7, 152.6, 133.0, 132.8, 130.1, 129.2, 129.1, 127.5, 125.9, 125.7, 125.5, 123.8, 115.7, 57.6, 54.6, 34.9, 31.2, 17.7. HRMS (ESI, m/z): Calculated for $C_{23}H_{22}N_4O_2Na$ $(M+Na)^+$ 409.1635, found 409.1635.

26. 9-([1,1'-biphenyl]-4-yl)-2-(azidomethyl)-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

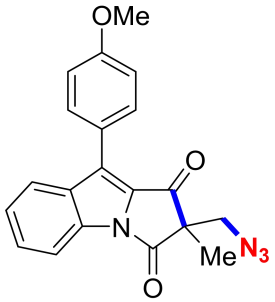
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 19.9 mg, yield 49 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.70-7.66 (m, 3H), 7.53 – 7.48 (m, 3H), 7.41 (d, J = 7.2 Hz, 1H), 3.92 (d, J = 12.0 Hz, 1H), 3.89 (d, J = 12.0 Hz, 1H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 169.7, 142.2, 140.4, 132.9, 132.8, 130.3, 129.9, 129.3, 129.1, 128.9, 127.7, 127.6, 127.1, 125.9, 125.0, 123.6, 115.7, 57.6, 54.6, 17.7. HRMS (ESI, m/z): Calculated for $C_{25}H_{19}N_4O_2$ $(M+H)^+$ 407.1503, found 407.1493.

27. 2-(azidomethyl)-9-(4-methoxyphenyl)-2-methyl-1H-pyrrolo[1,2-a]indole-1,3(2H)-dione

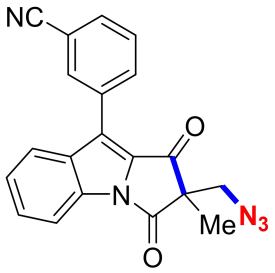
A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 20.2 mg, yield 56 %.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.93 – 7.91 (m, 2H), 7.67-7.63 (m, 1H), 7.49 – 7.45 (m, 1H), 7.11 – 7.08 (m, 2H), 3.90 (s, 3H), 3.88 (d, J = 3.4 Hz, 2H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 169.6, 160.5, 133.0, 132.8, 130.9, 129.2, 125.7, 125.5, 123.7, 122.8, 115.7, 114.3, 57.6, 55.4, 54.6, 17.7. HRMS (ESI, m/z): Calculated for $C_{20}H_{16}N_4O_3Na$ $(M+Na)^+$ 383.1115, found 383.1114.

28. 3-(2-(azidomethyl)-2-methyl-1,3-dioxo-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)benzonitrile

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20:1), 15.6 mg, yield 44 %.

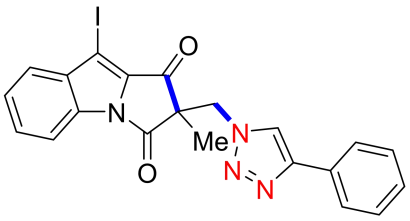


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.21 – 8.18 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.55-7.51 (m, 1H), 3.90 (s, 2H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 169.6, 133.7, 132.6, 132.5, 132.2, 131.8, 130.9, 129.8, 129.6, 126.3, 122.8, 122.1, 118.4, 115.9, 113.2, 57.5, 54.6, 17.5. HRMS (ESI, m/z): Calculated for $C_{20}H_{13}N_5O_2Na$ $(M+Na)^+$ 378.0961, found 378.0960.

29.

8-iodo-2-methyl-2-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)cyclopenta[a]indene-1,3(2H,3aH)-dione

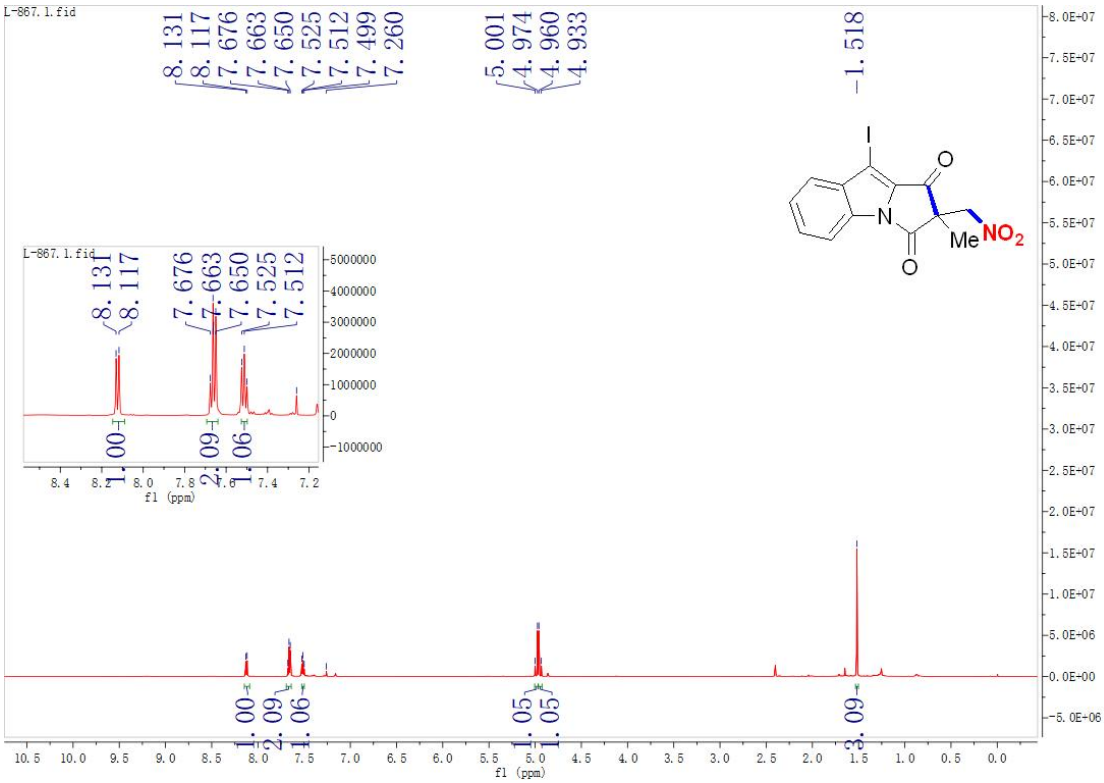
A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10:1), 30.5 mg, yield 73 %. Mp: 224-225 °C.



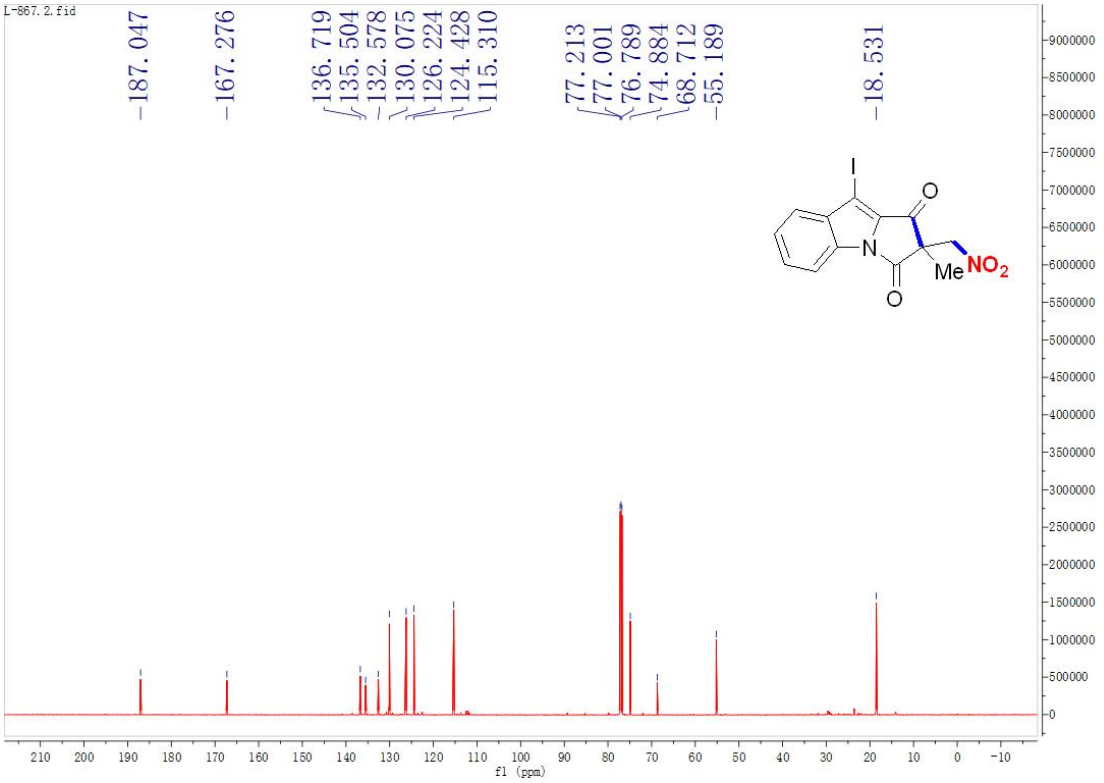
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.60 (dd, *J* = 14.4, 7.6 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 4.89 (d, *J* = 14.0 Hz, 1H), 4.84 (d, *J* = 14.0 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.3, 167.9, 147.9, 136.9, 135.5, 132.4, 130.0, 129.9, 128.7, 128.3, 126.2, 125.7, 124.3, 120.6, 115.4, 68.3, 57.6, 51.6, 19.5. HRMS (ESI, m/z): Calculated for $C_{21}H_{15}IN_4O_2Na$ $(M+Na)^+$ 505.0132, found 505.0132.

Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR

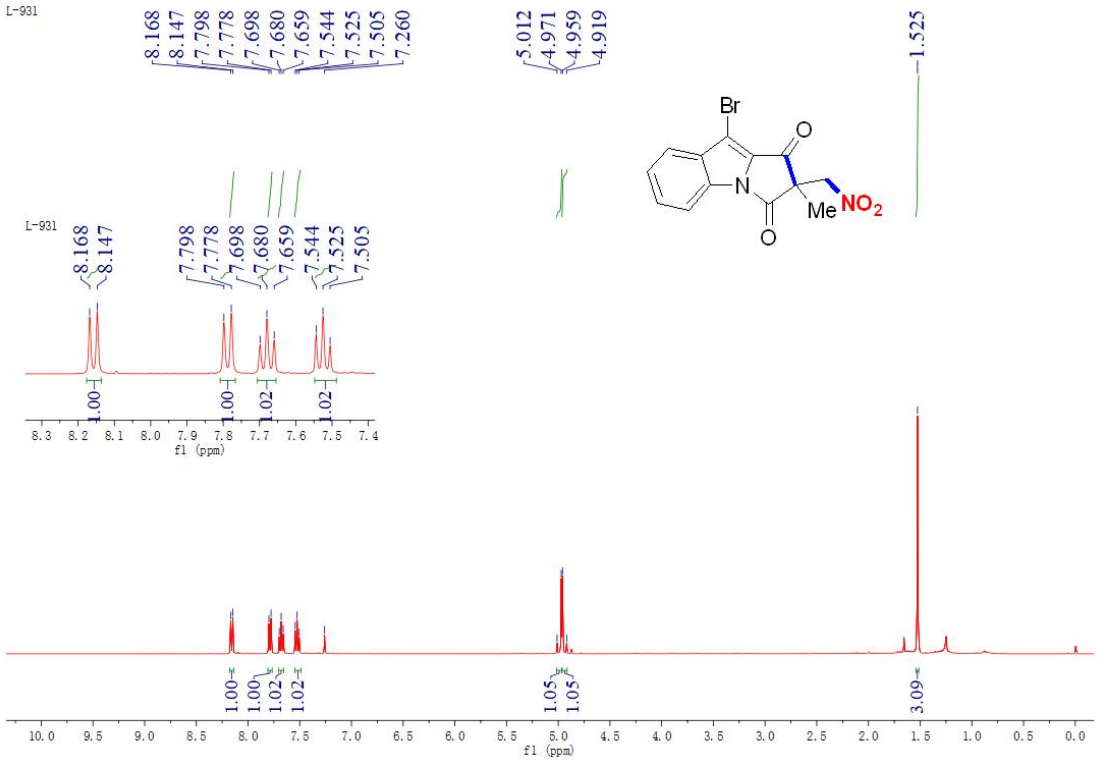
1-^{1}H NMR (600 MHz, $CDCl_3$)



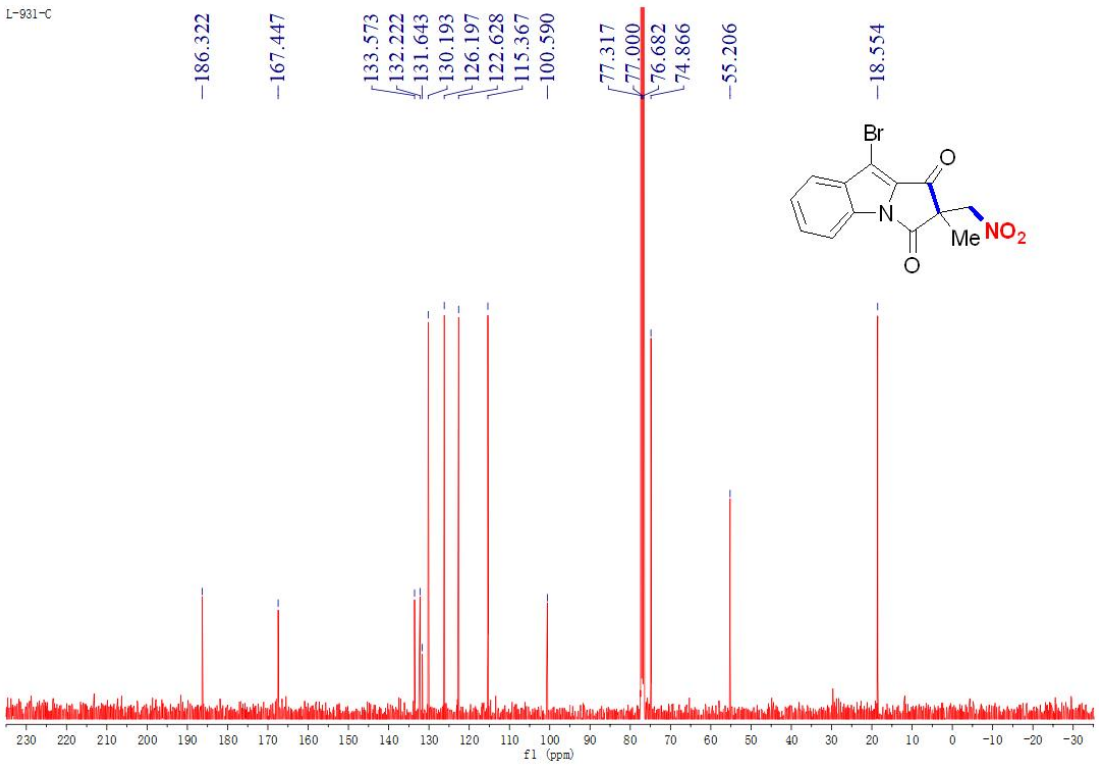
1-^{13}C NMR (150 MHz, $CDCl_3$)



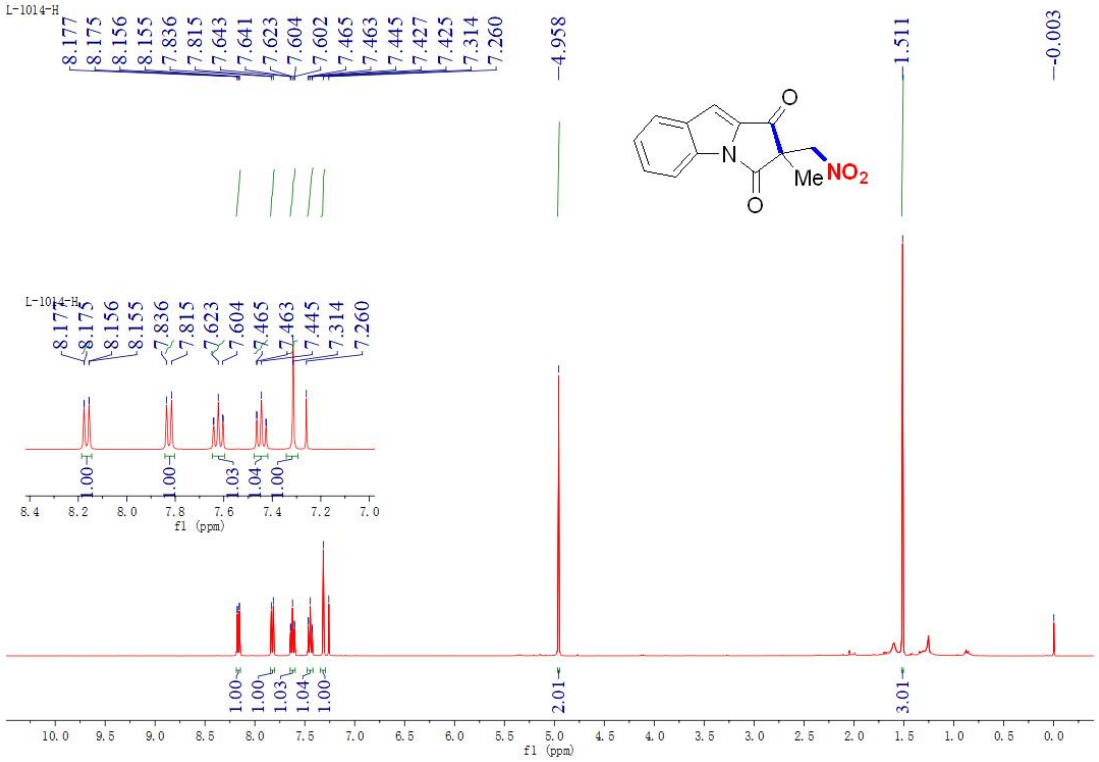
2-^{1}H NMR (400 MHz, $CDCl_3$)



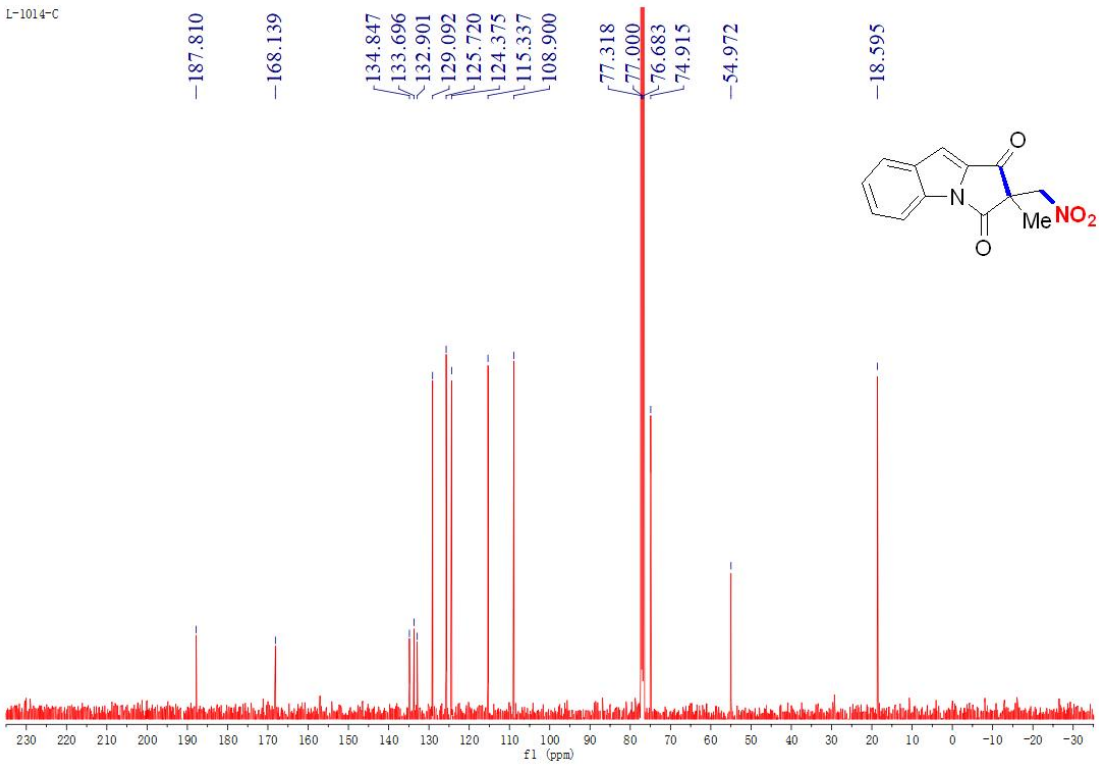
2-^{13}C NMR (100 MHz, $CDCl_3$)



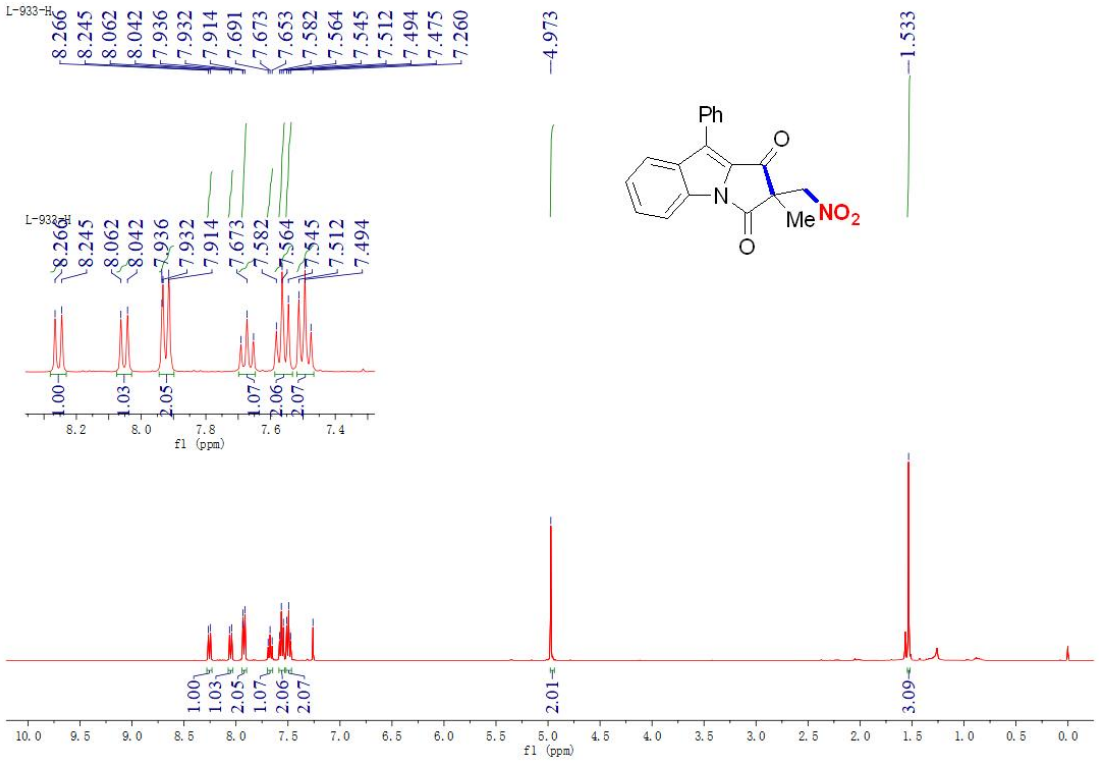
3-^{1}H NMR (400 MHz, $CDCl_3$)



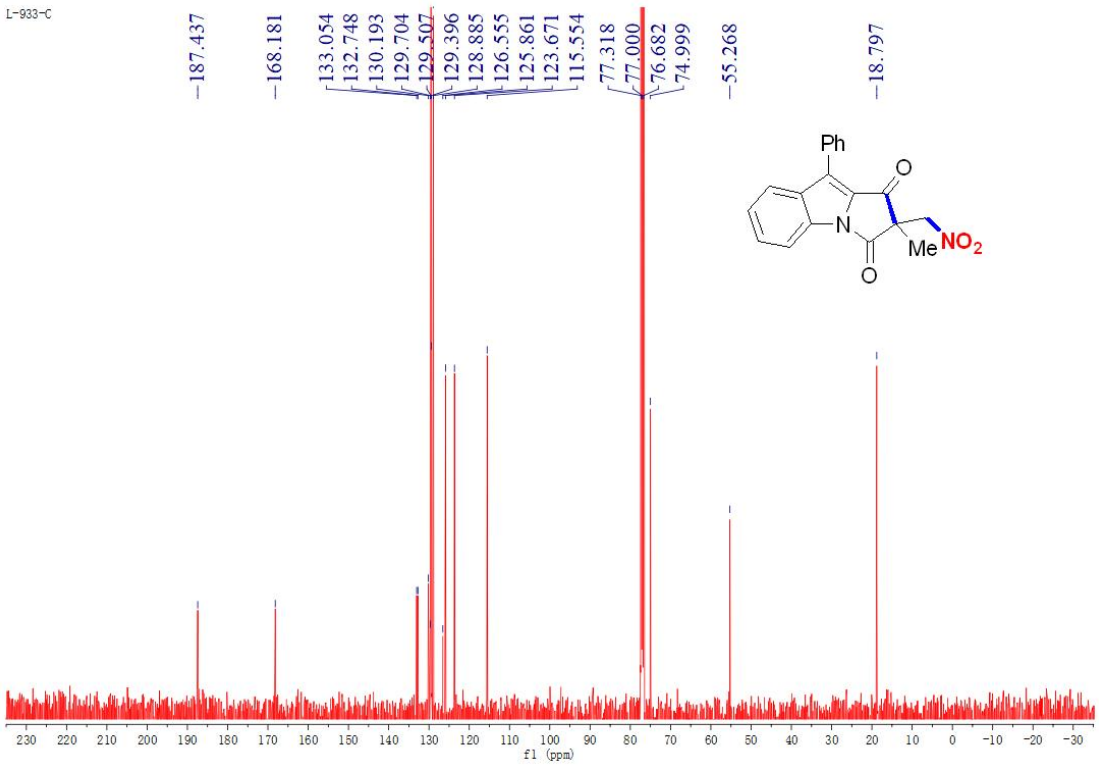
3-^{13}C NMR (100 MHz, $CDCl_3$)



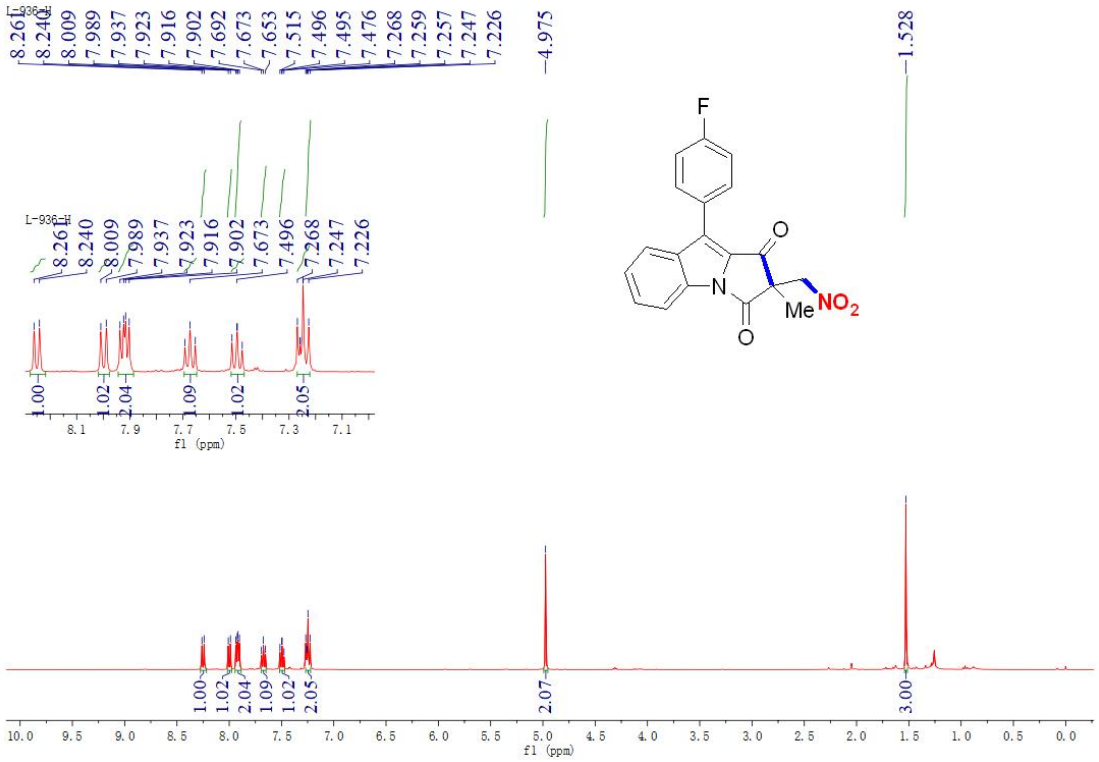
4-^{1}H NMR (400 MHz, $CDCl_3$)



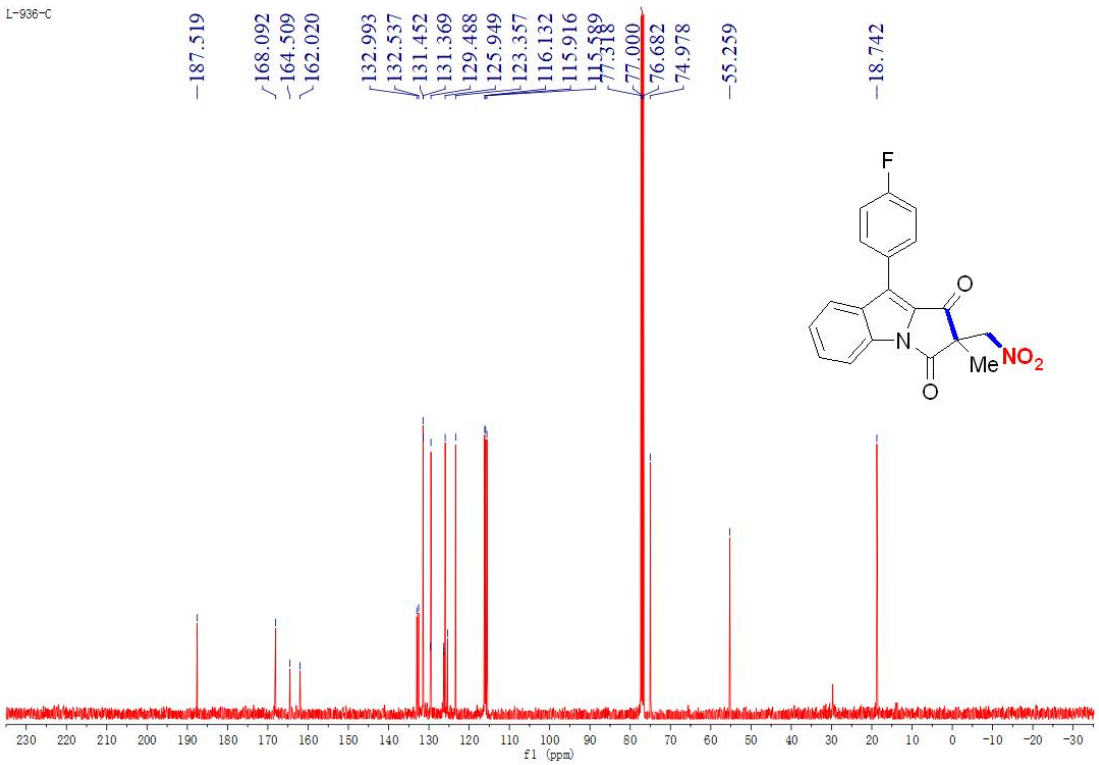
4-^{13}C NMR (100 MHz, $CDCl_3$)



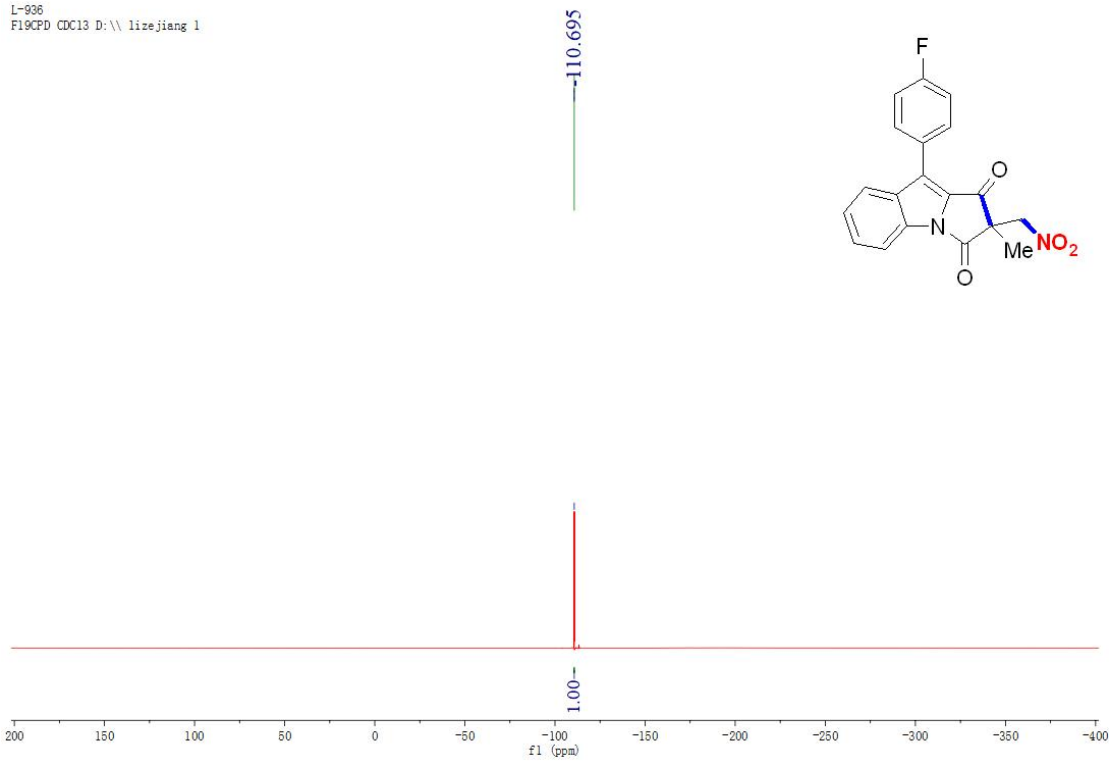
5-^{1}H NMR (400 MHz, $CDCl_3$)



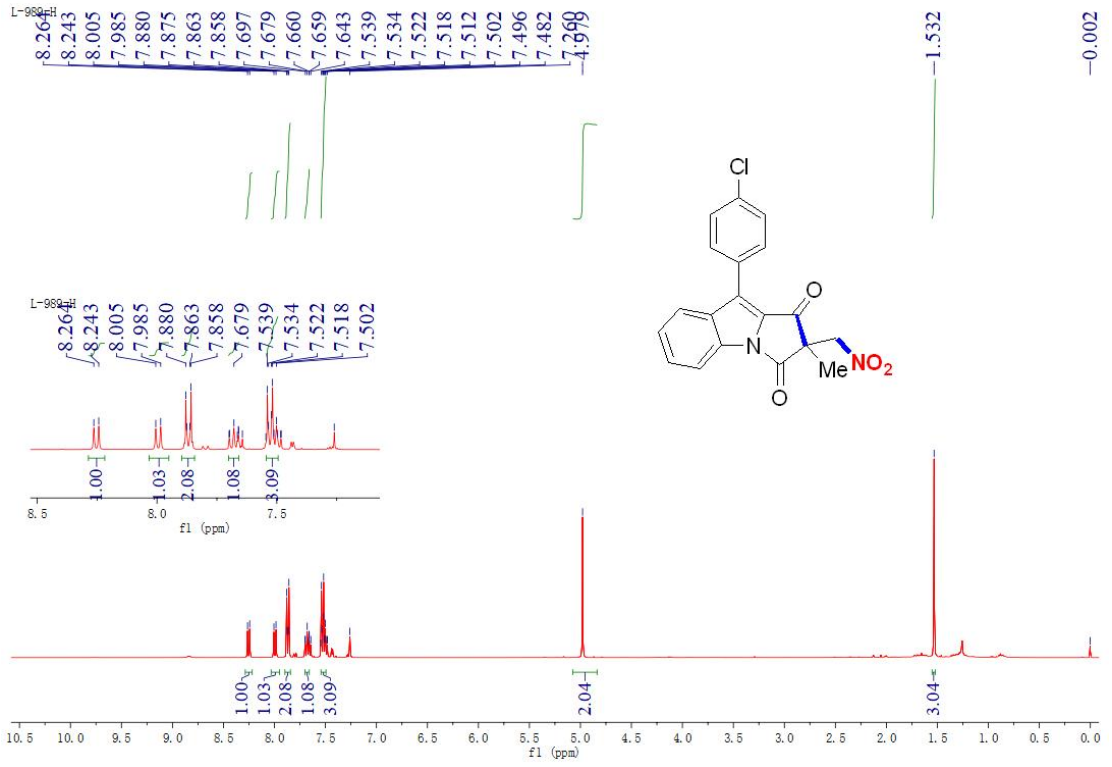
5-^{13}C NMR (100 MHz, $CDCl_3$)



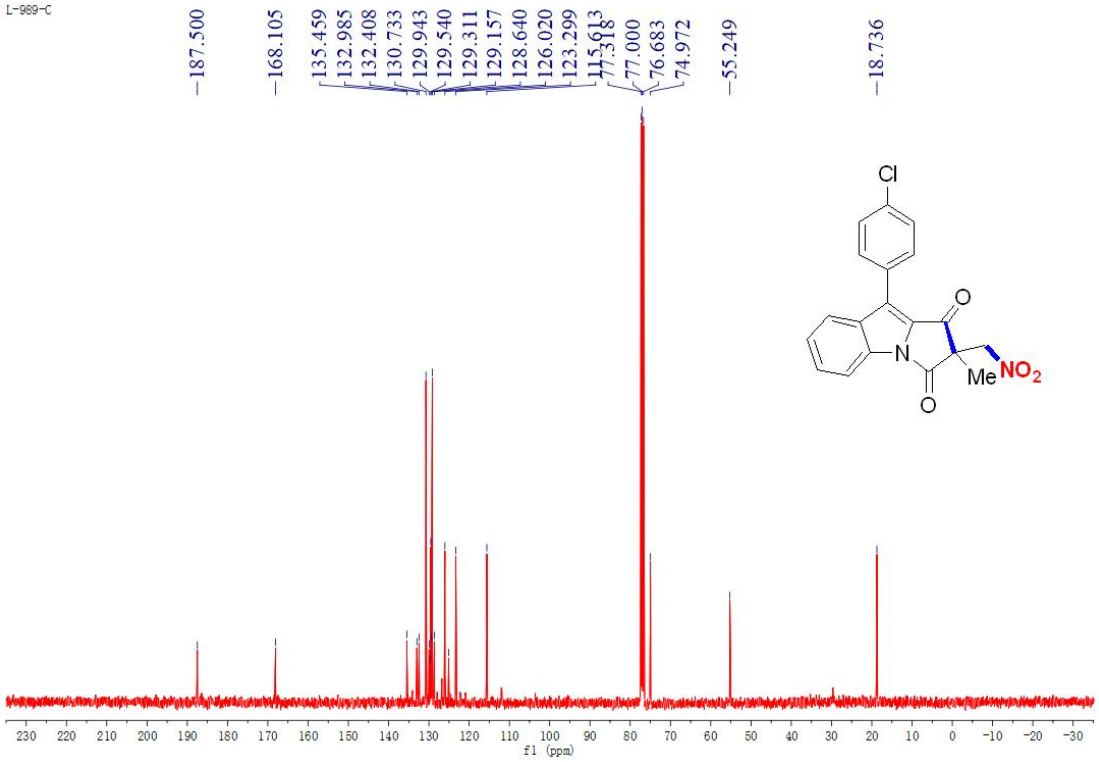
5-^{19}F NMR (565 MHz, $CDCl_3$)



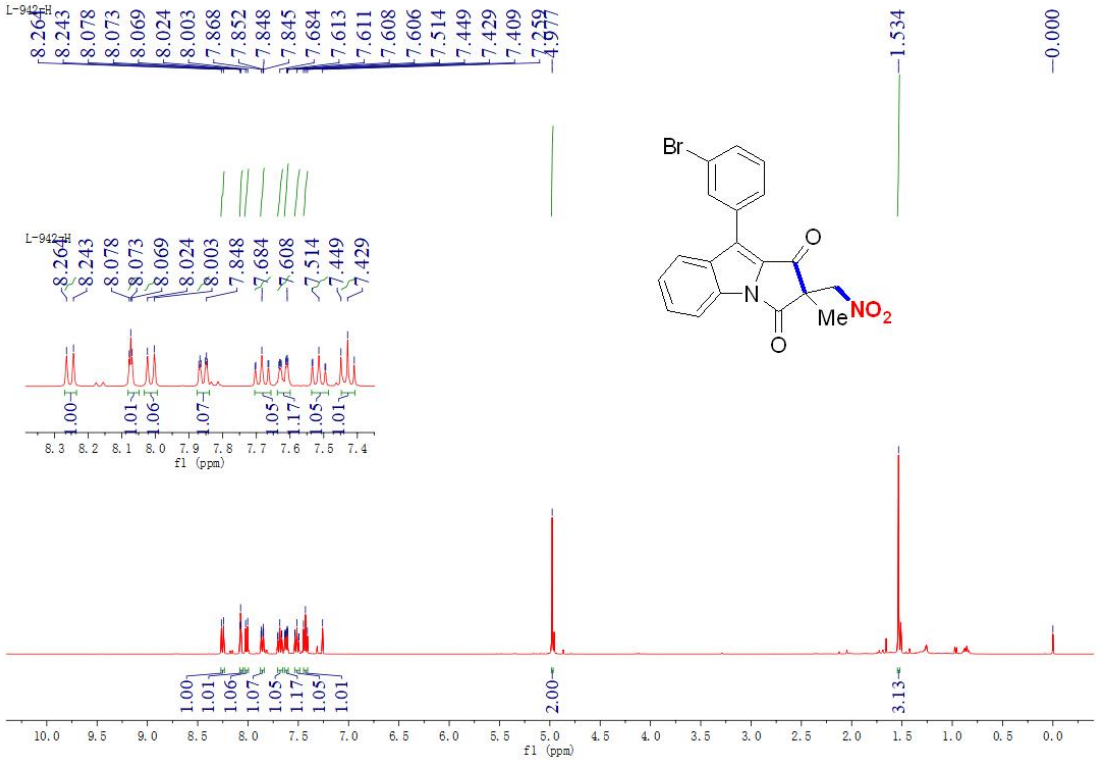
6-^{1}H NMR (400 MHz, $CDCl_3$)



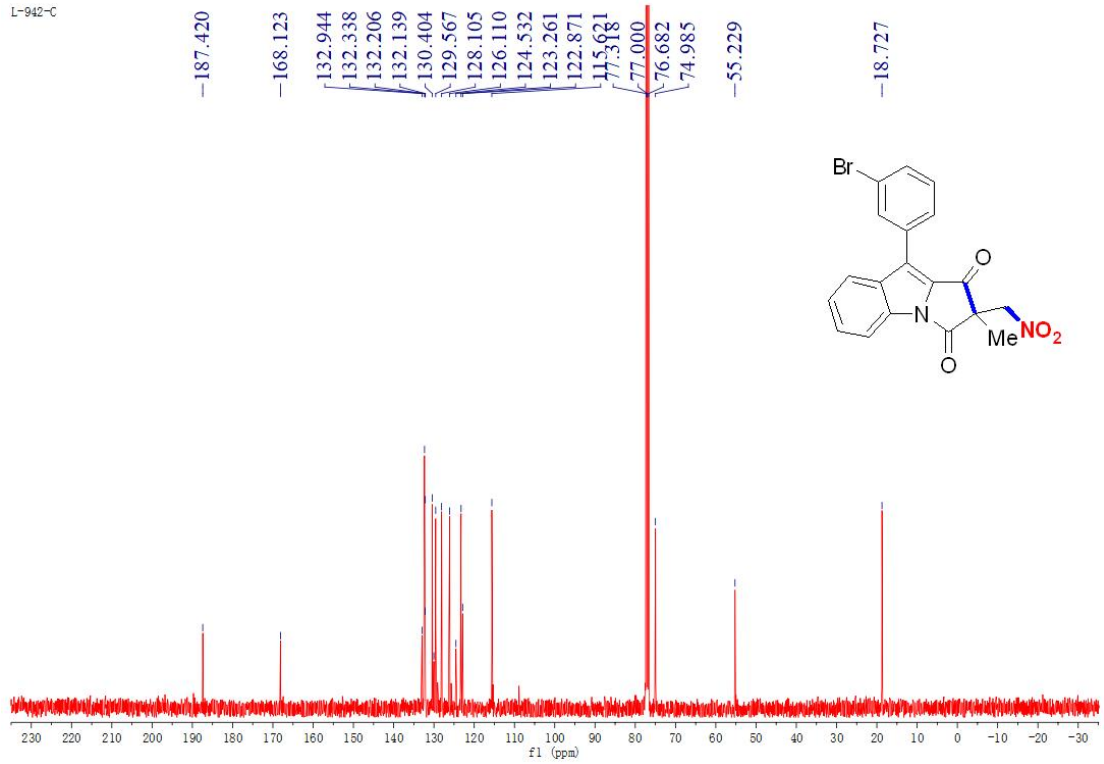
6-^{13}C NMR (100 MHz, $CDCl_3$)



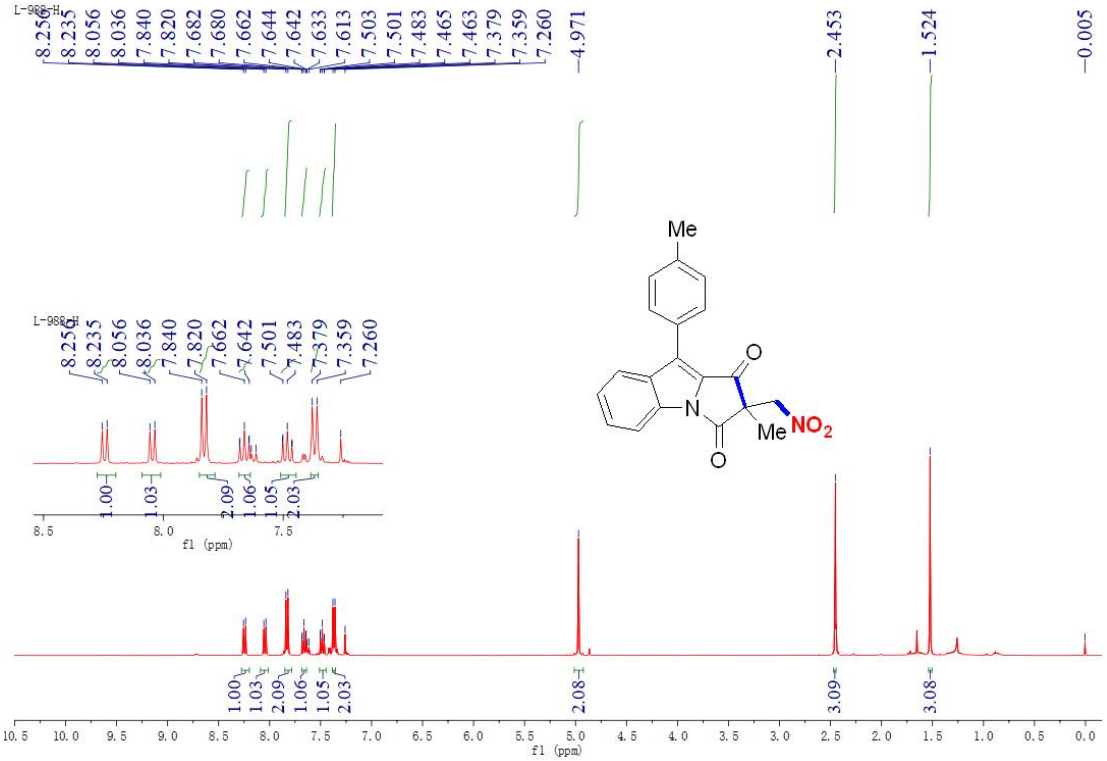
7-^{1}H NMR (400 MHz, $CDCl_3$)



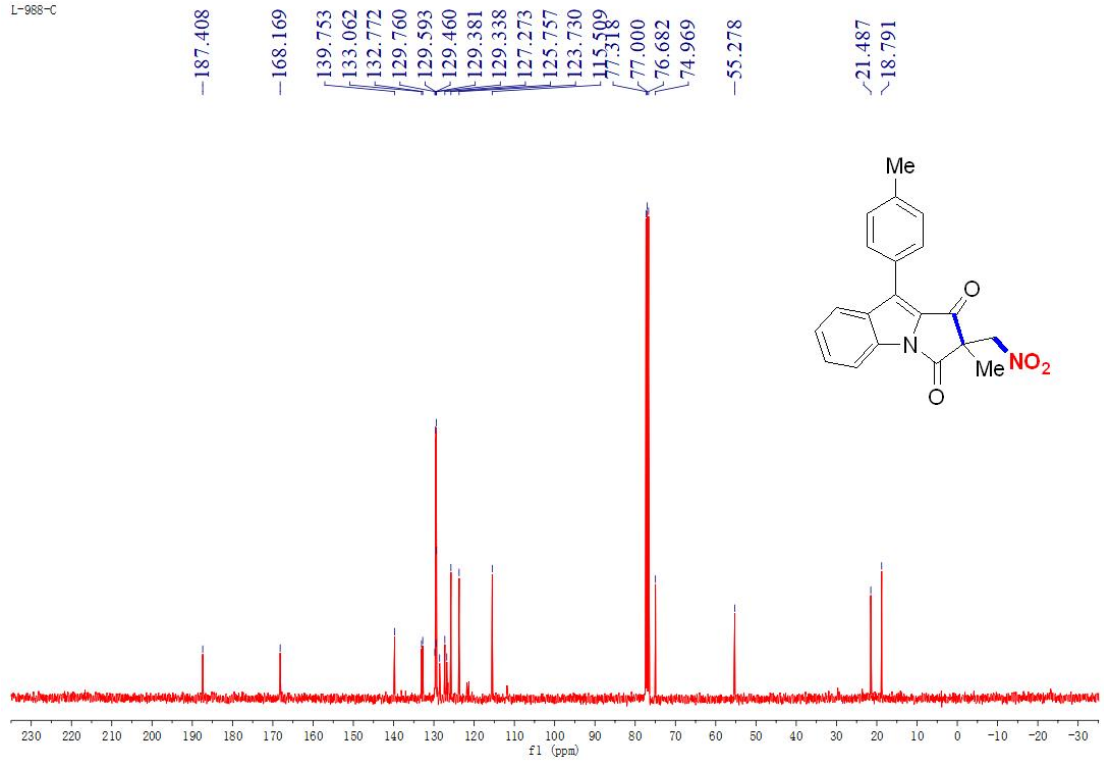
7-^{13}C NMR (100 MHz, $CDCl_3$)



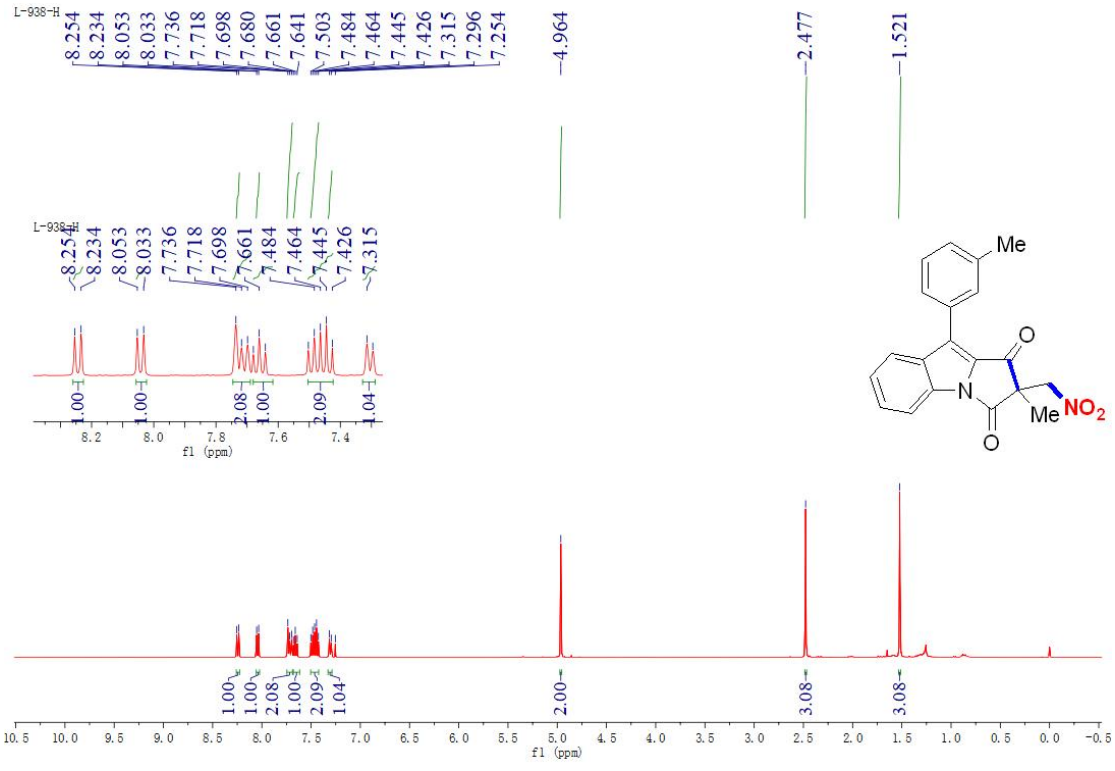
8-^{1}H NMR (400 MHz, $CDCl_3$)



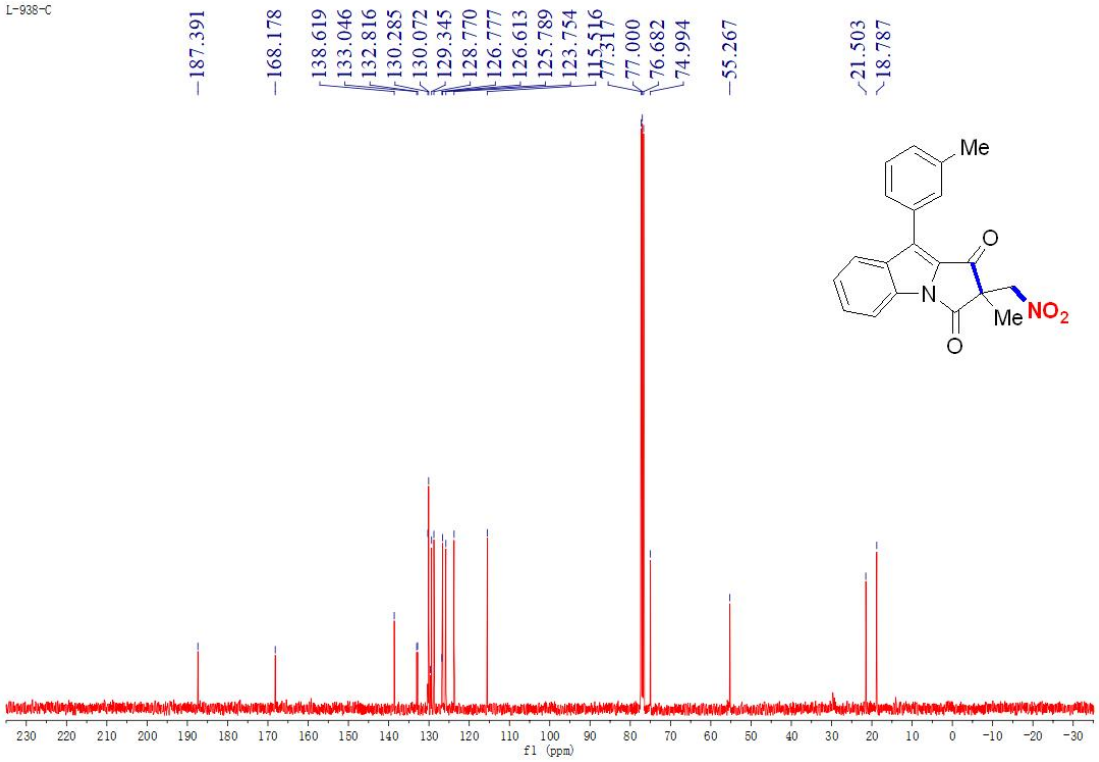
8-^{13}C NMR (100 MHz, $CDCl_3$)



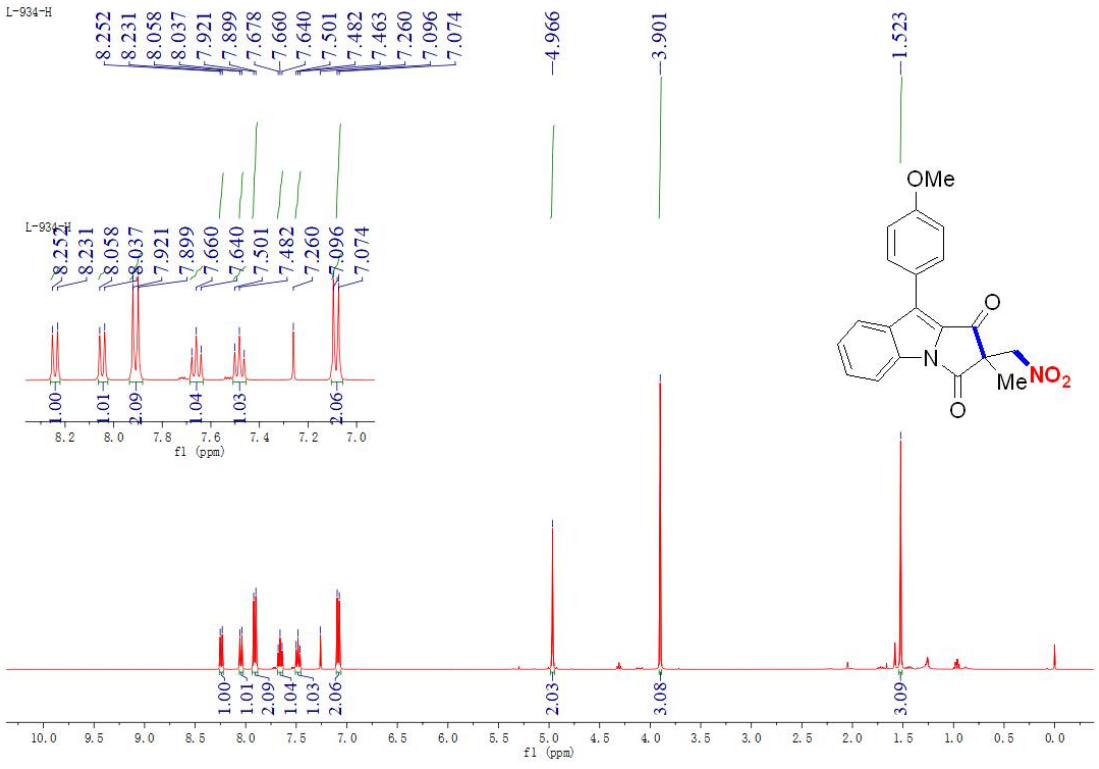
9-^{1}H NMR (400 MHz, $CDCl_3$)



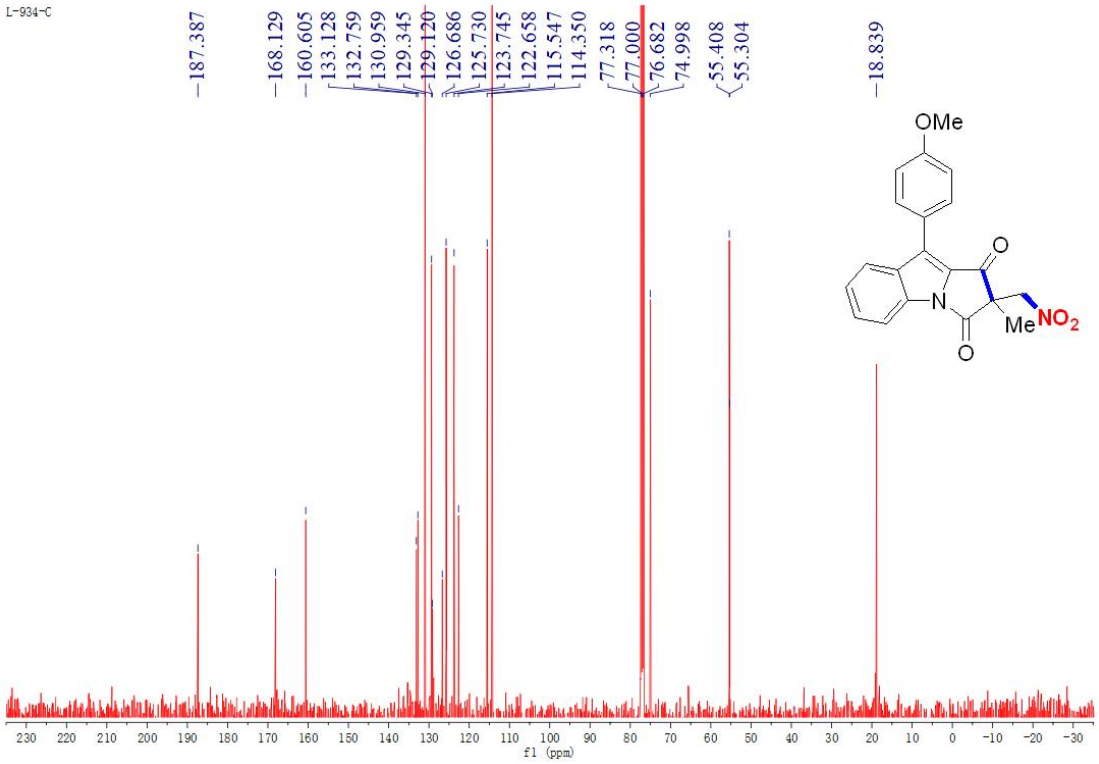
9-^{13}C NMR (100 MHz, $CDCl_3$)



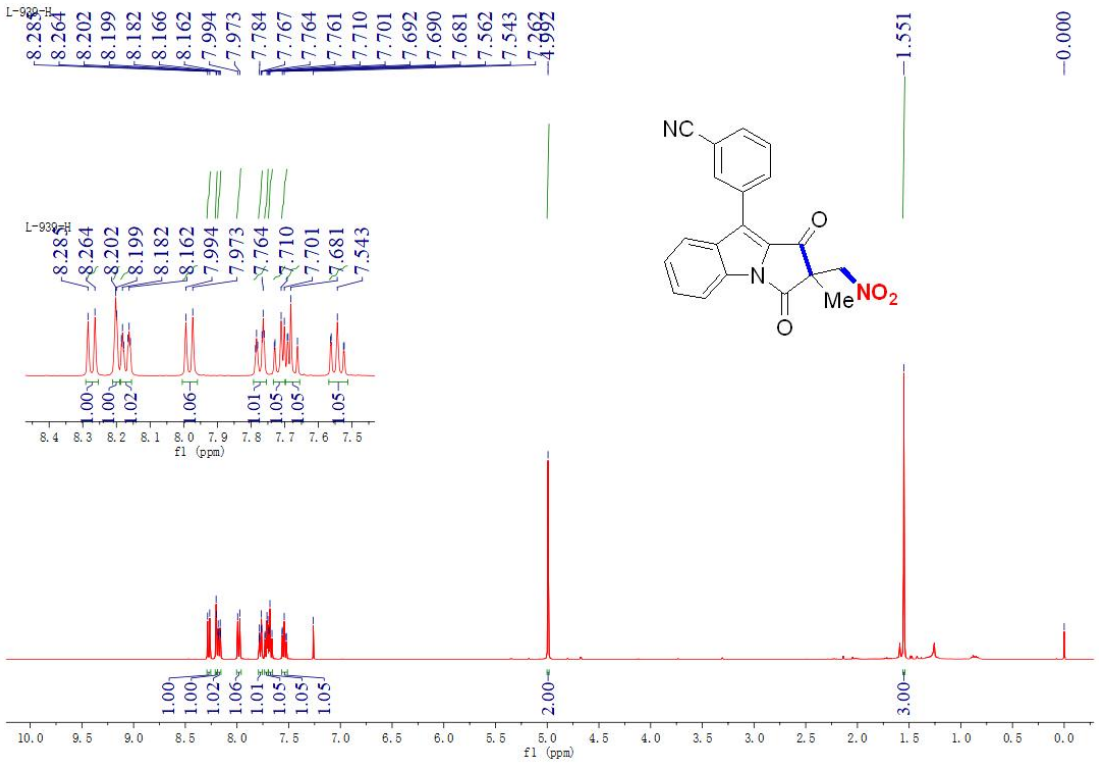
10-^{1}H NMR (400 MHz, $CDCl_3$)



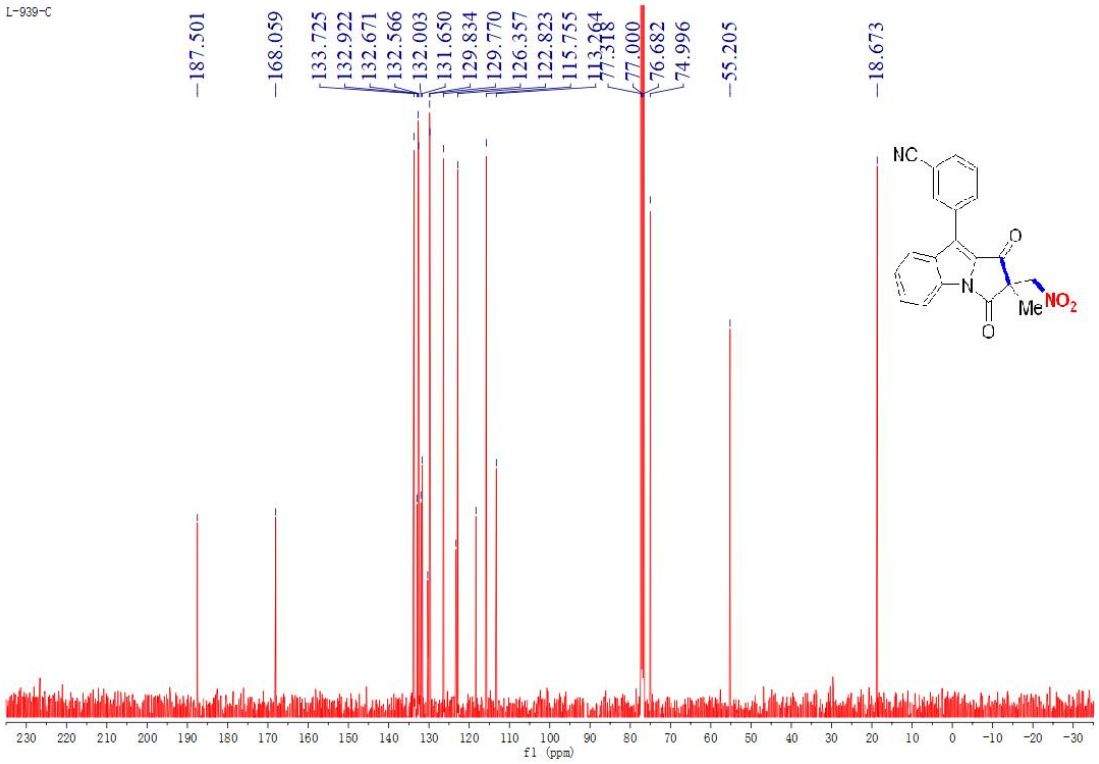
10-^{13}C NMR (100 MHz, $CDCl_3$)



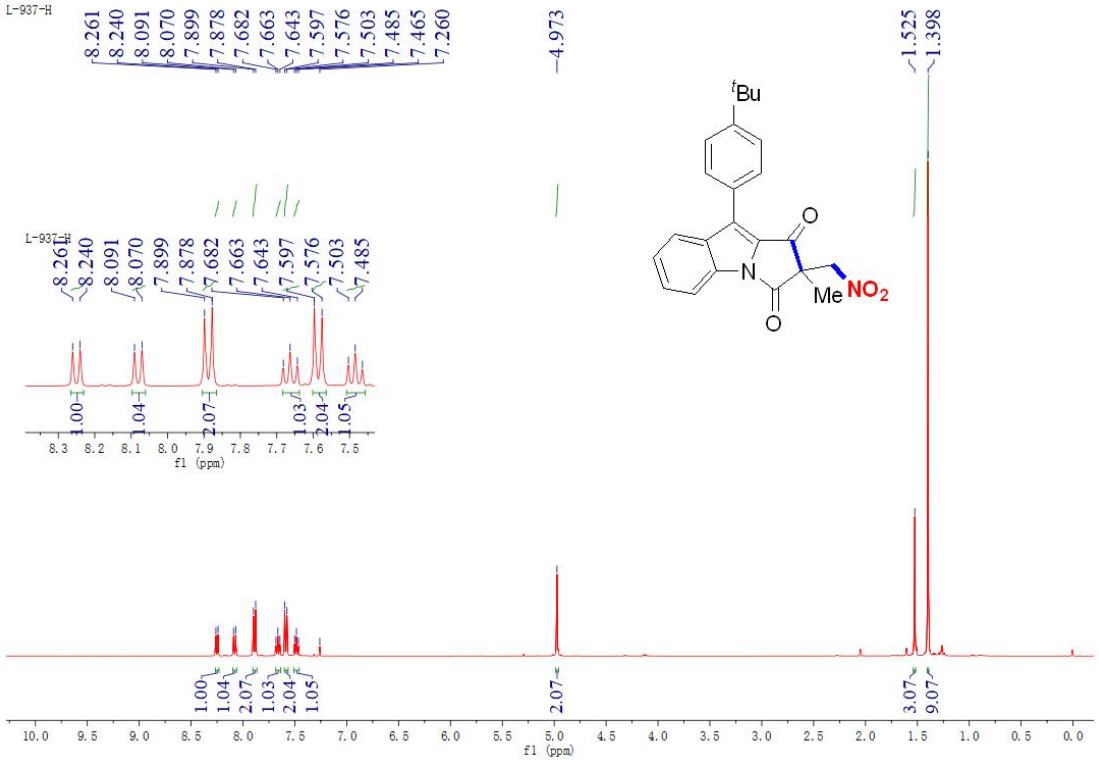
11-^{1}H NMR (400 MHz, $CDCl_3$)



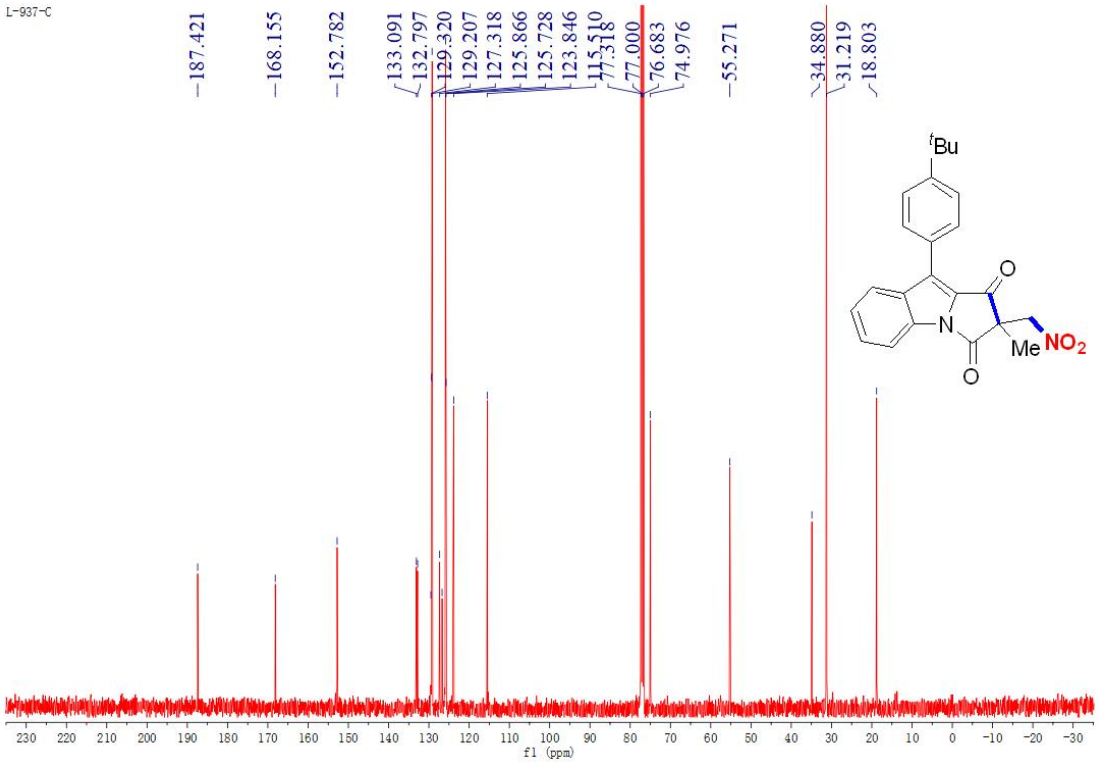
11-^{13}C NMR (100 MHz, $CDCl_3$)



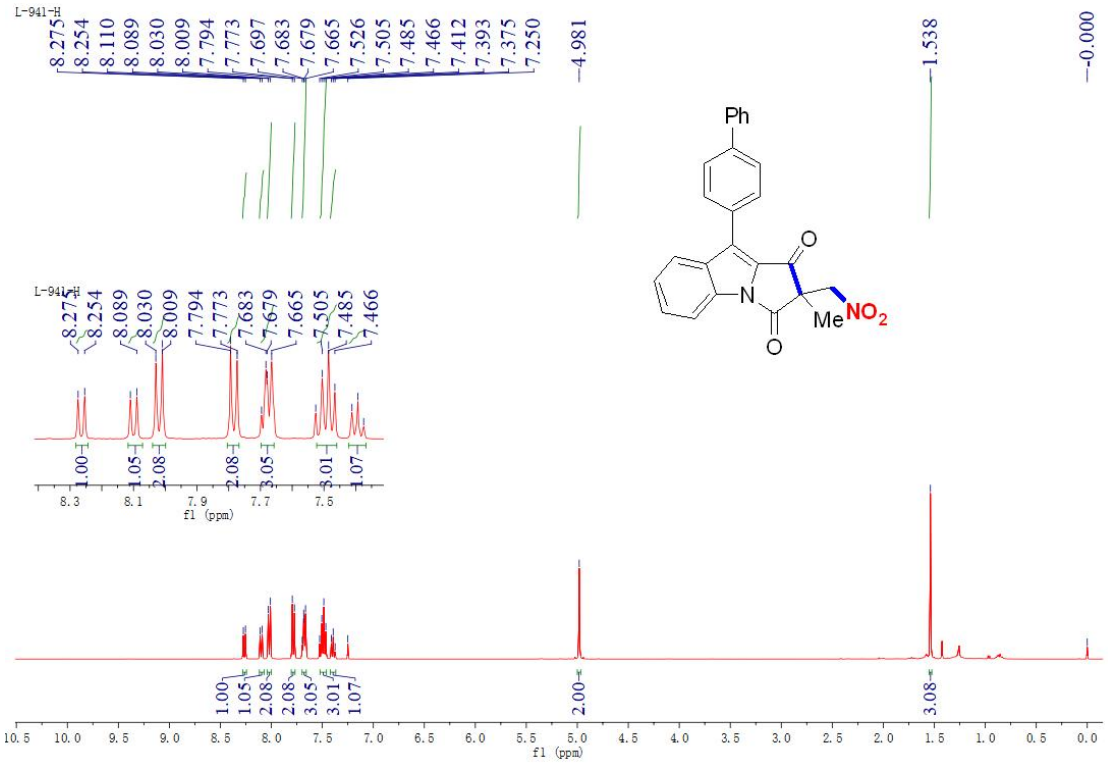
12-^{1}H NMR (400 MHz, $CDCl_3$)



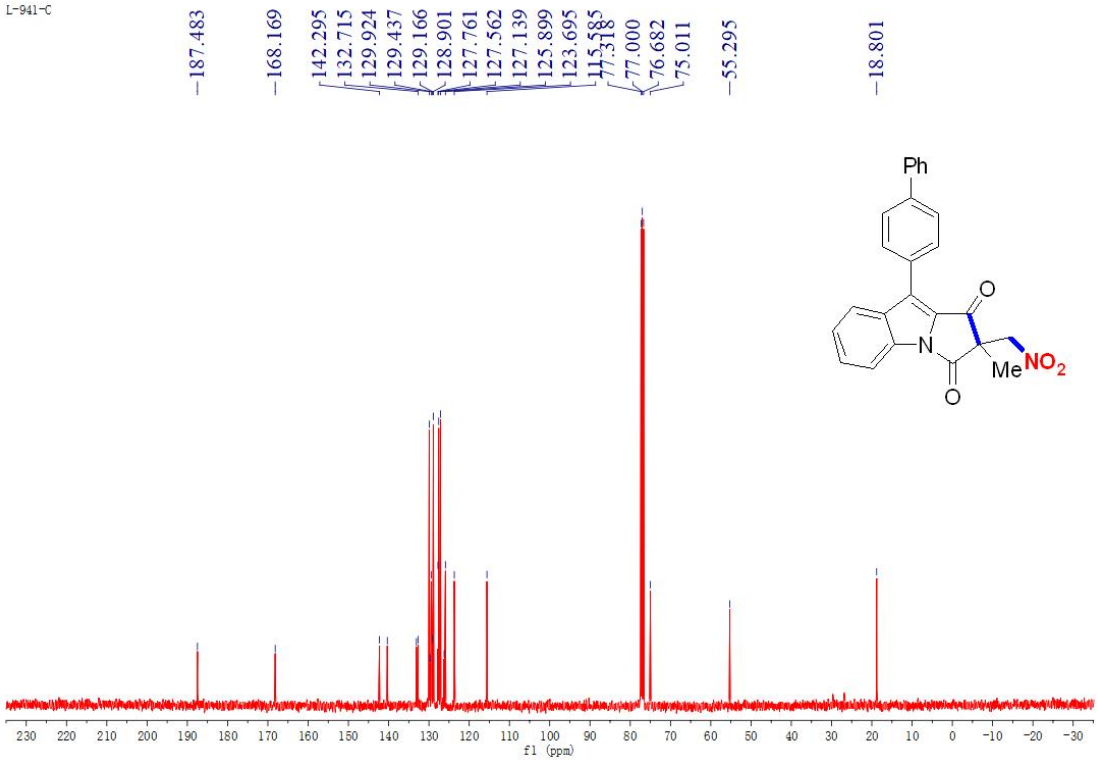
12-^{13}C NMR (100 MHz, $CDCl_3$)



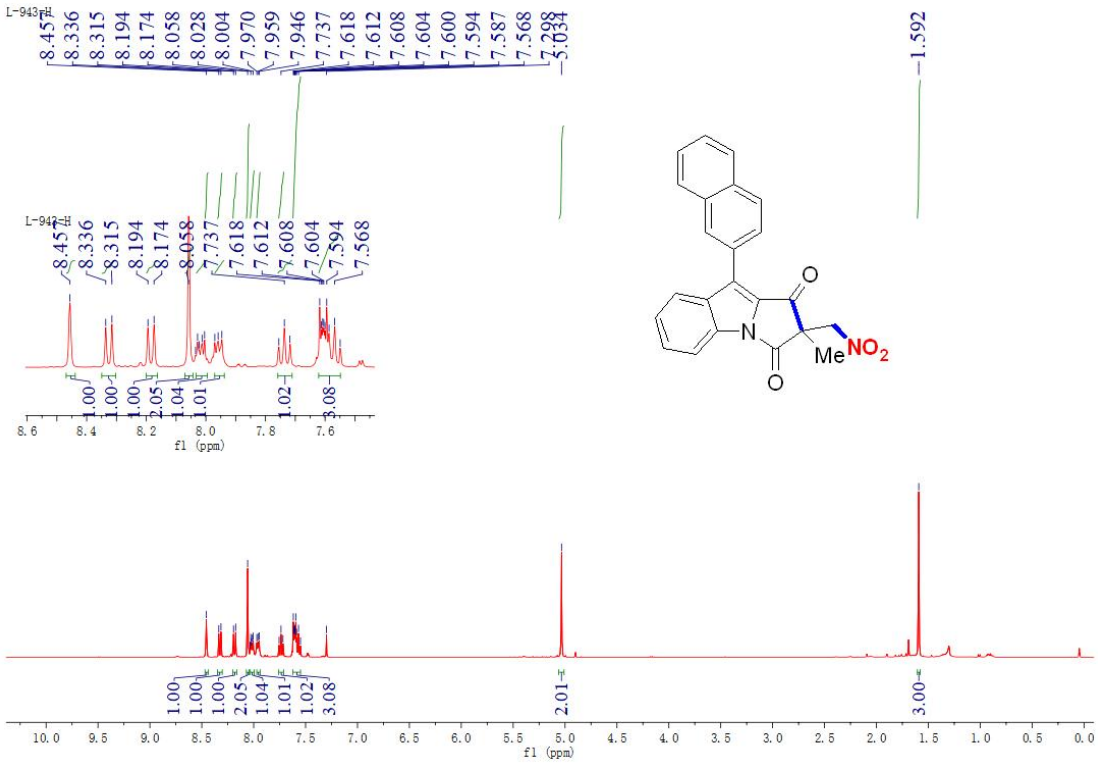
13-^{1}H NMR (400 MHz, $CDCl_3$)



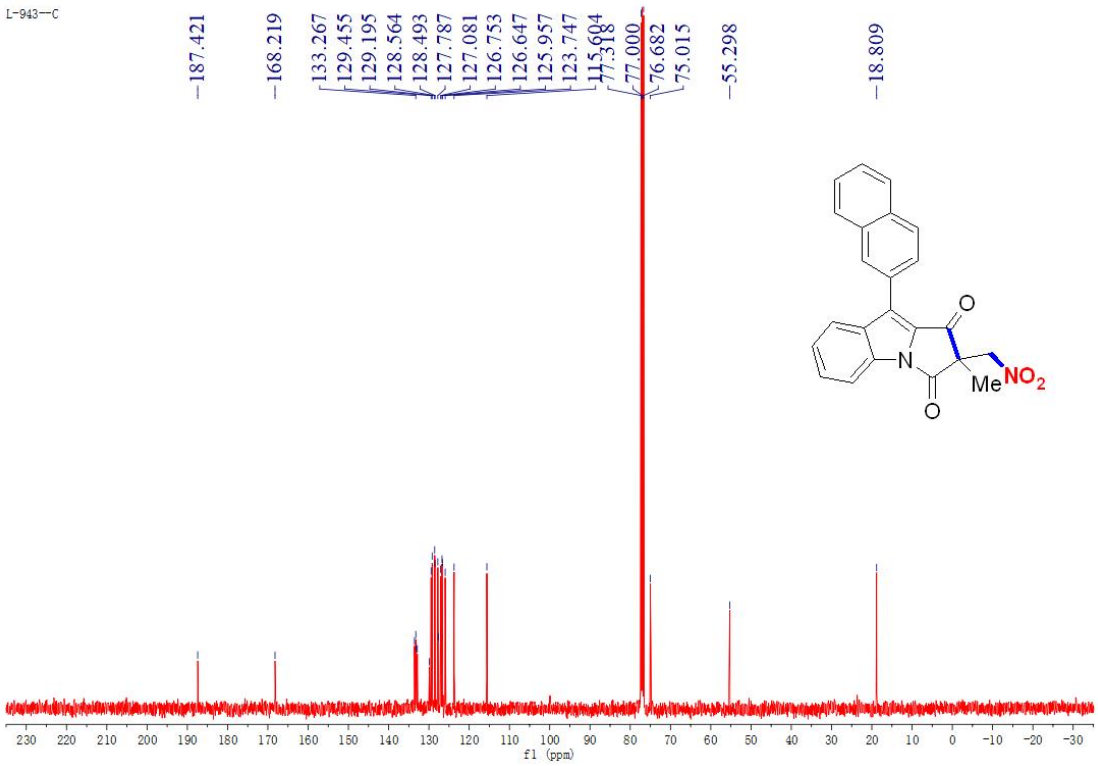
13-^{13}C NMR (100 MHz, $CDCl_3$)



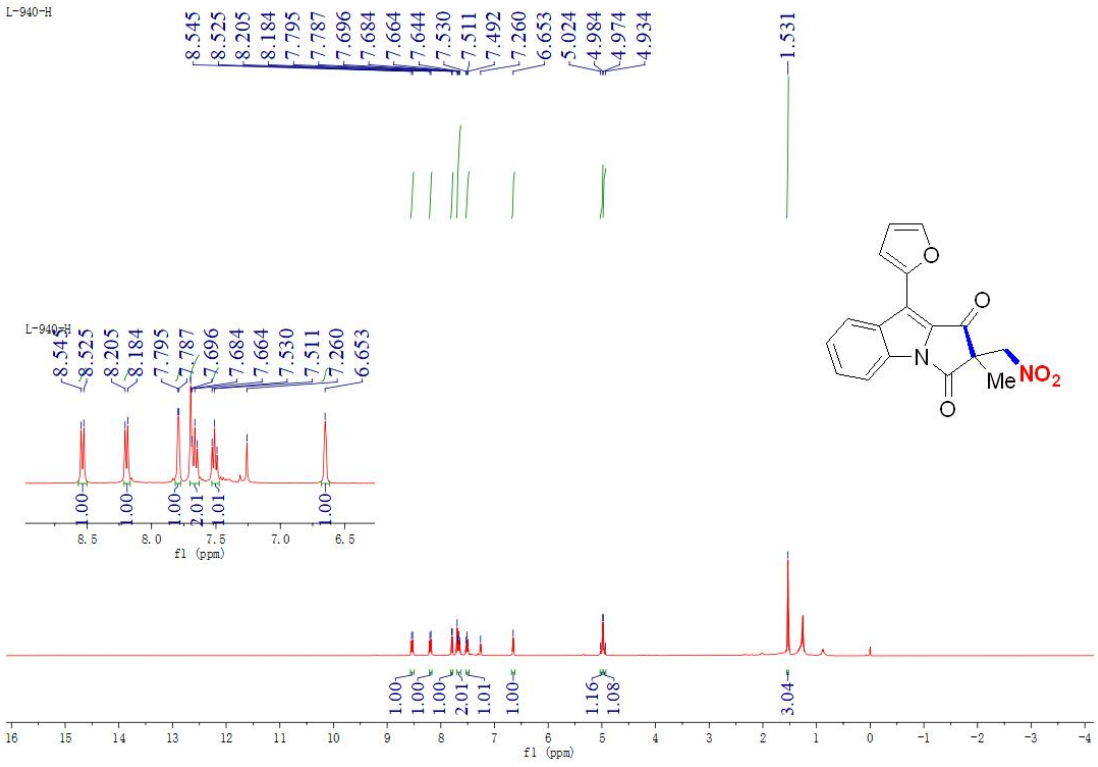
14-^{1}H NMR (400 MHz, $CDCl_3$)



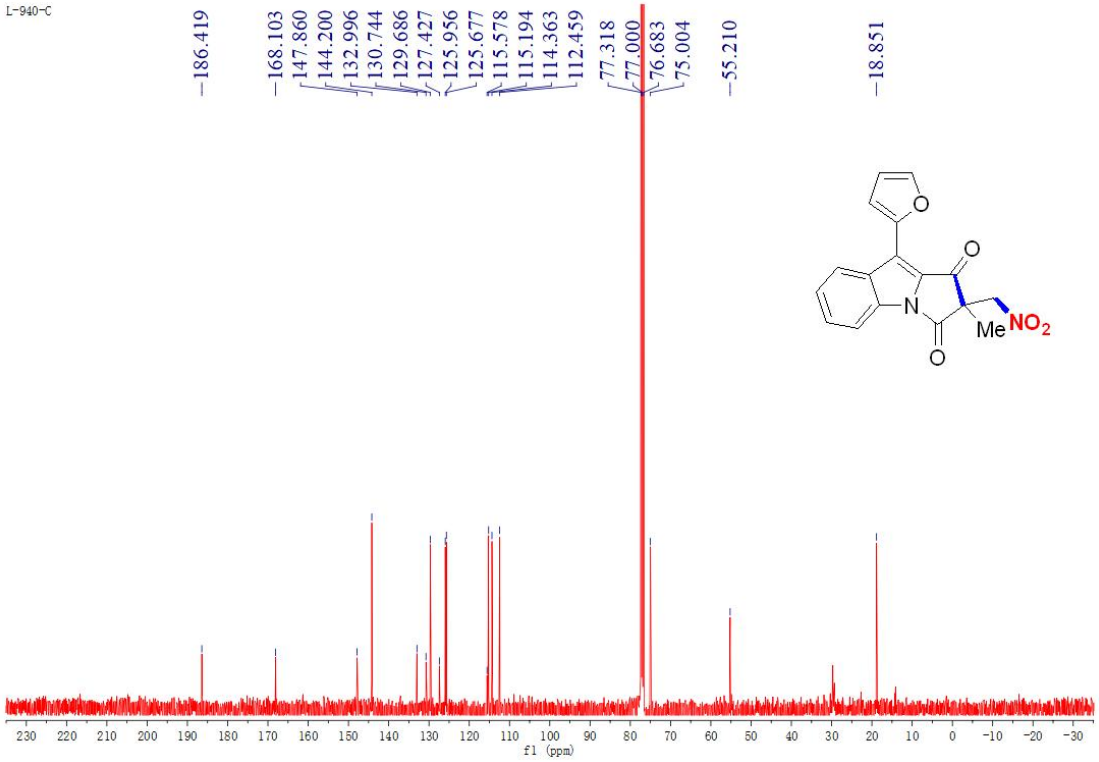
14-^{13}C NMR (100 MHz, $CDCl_3$)



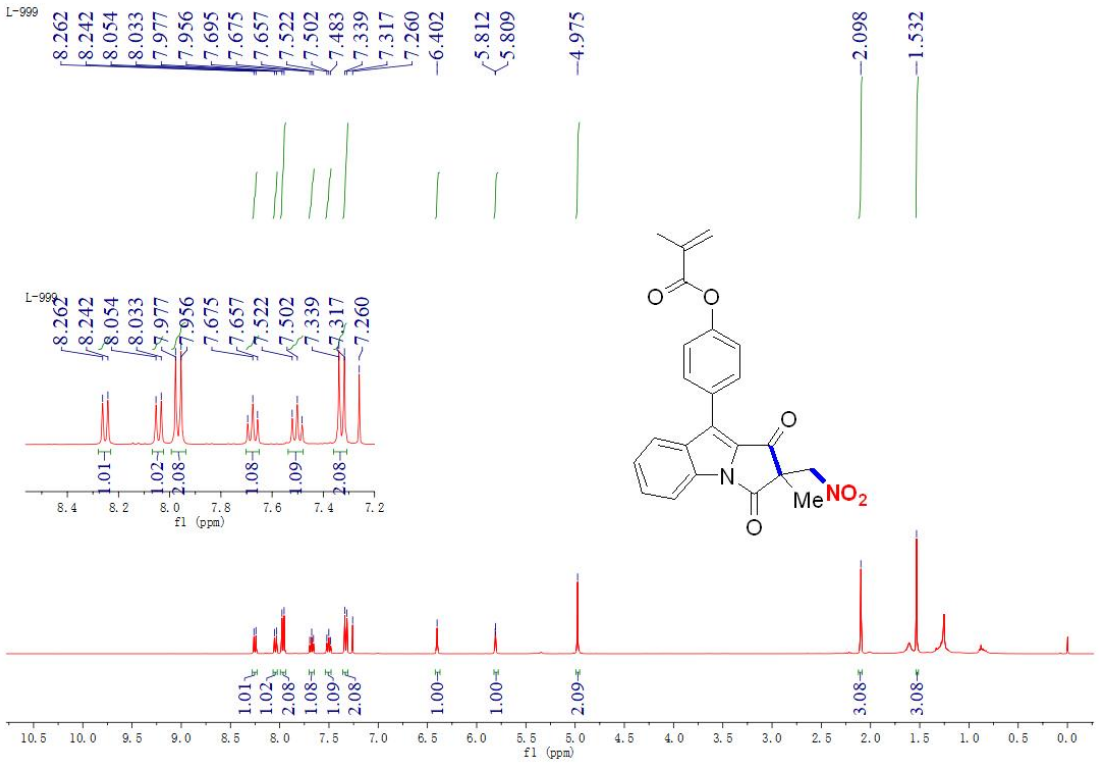
15-^{1}H NMR (400 MHz, $CDCl_3$)



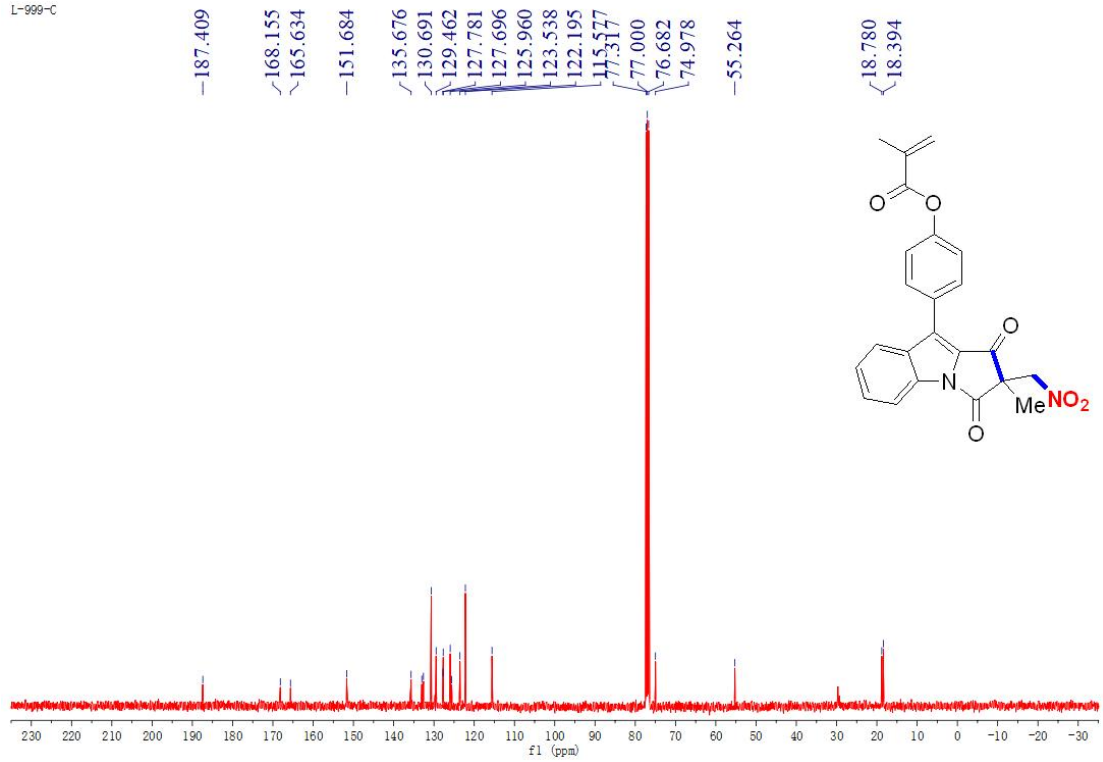
15-^{13}C NMR (100 MHz, $CDCl_3$)



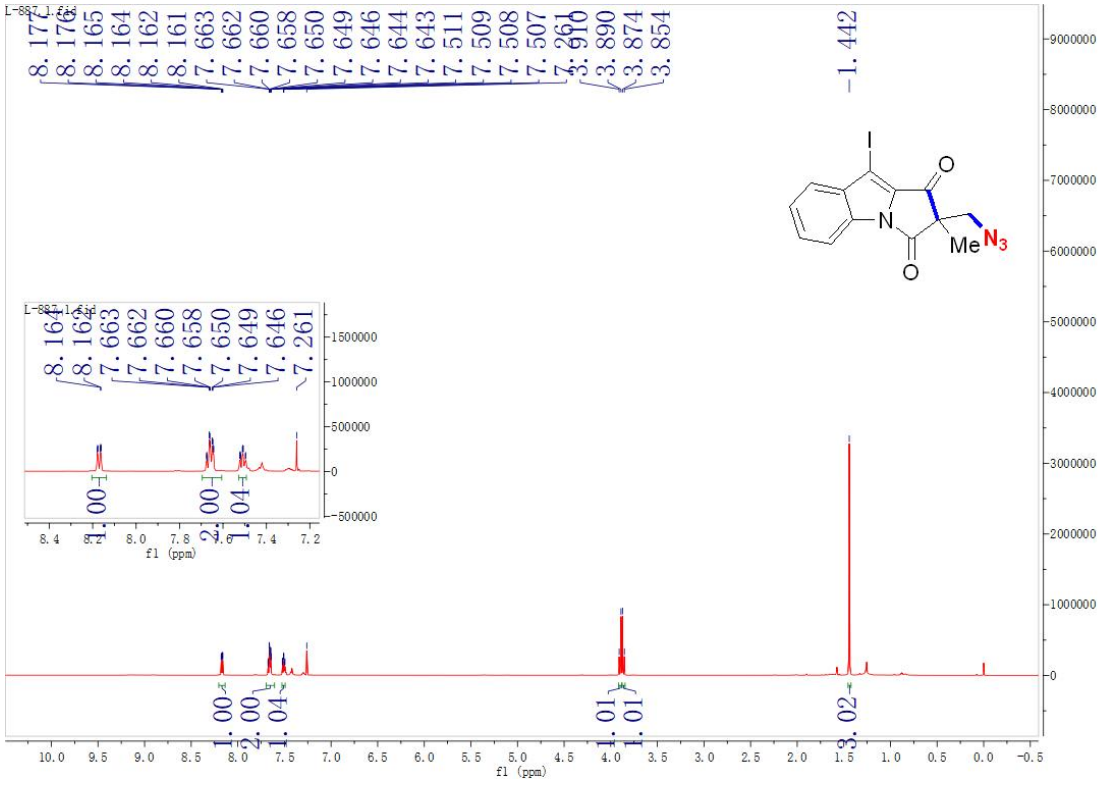
16-^{1}H NMR (400 MHz, $CDCl_3$)



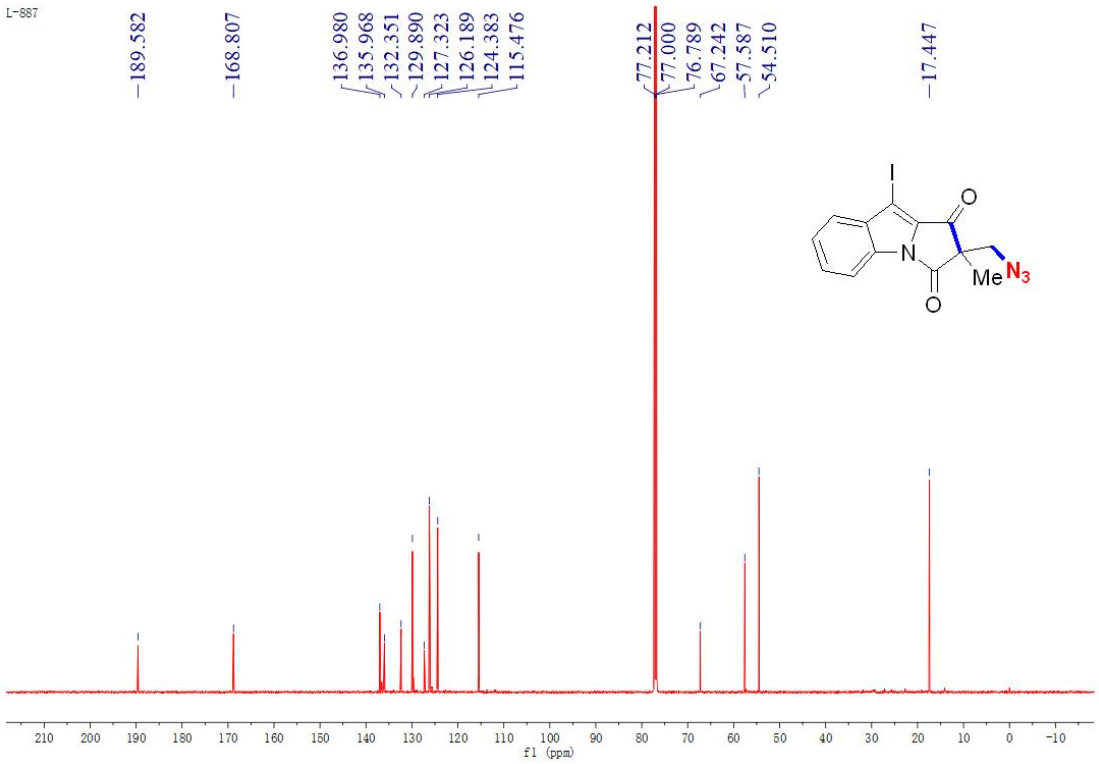
16-^{13}C NMR (100 MHz, $CDCl_3$)



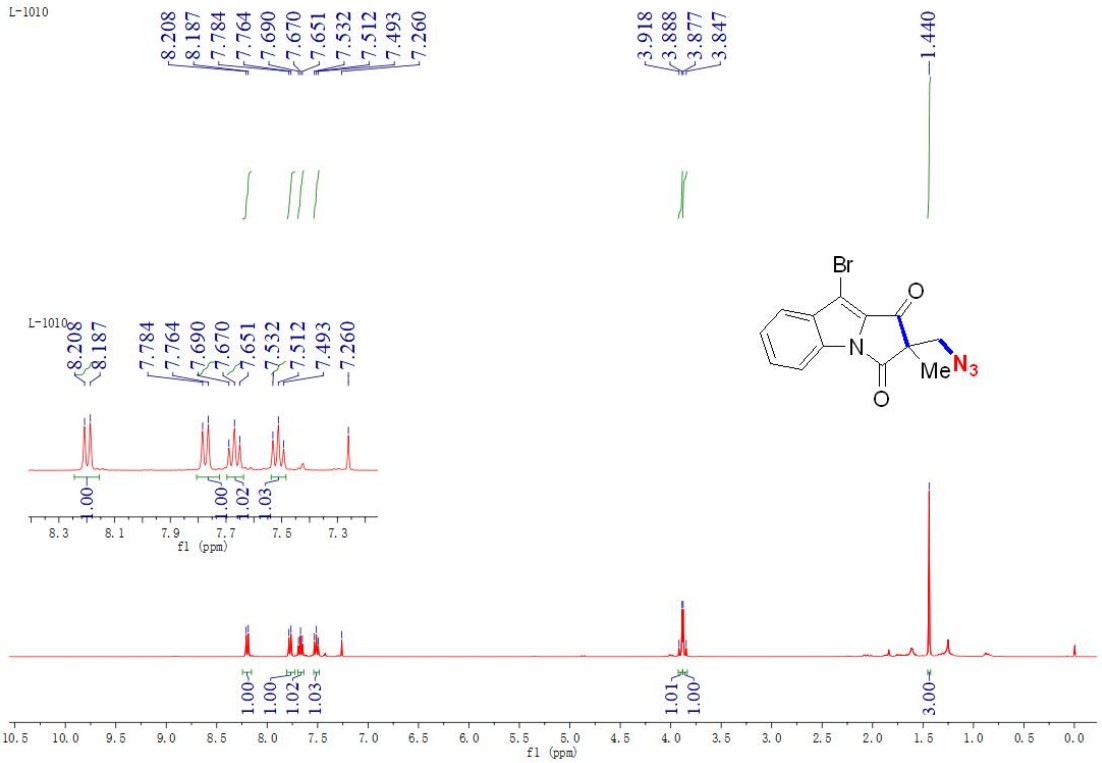
17-^{1}H NMR (600 MHz, $CDCl_3$)



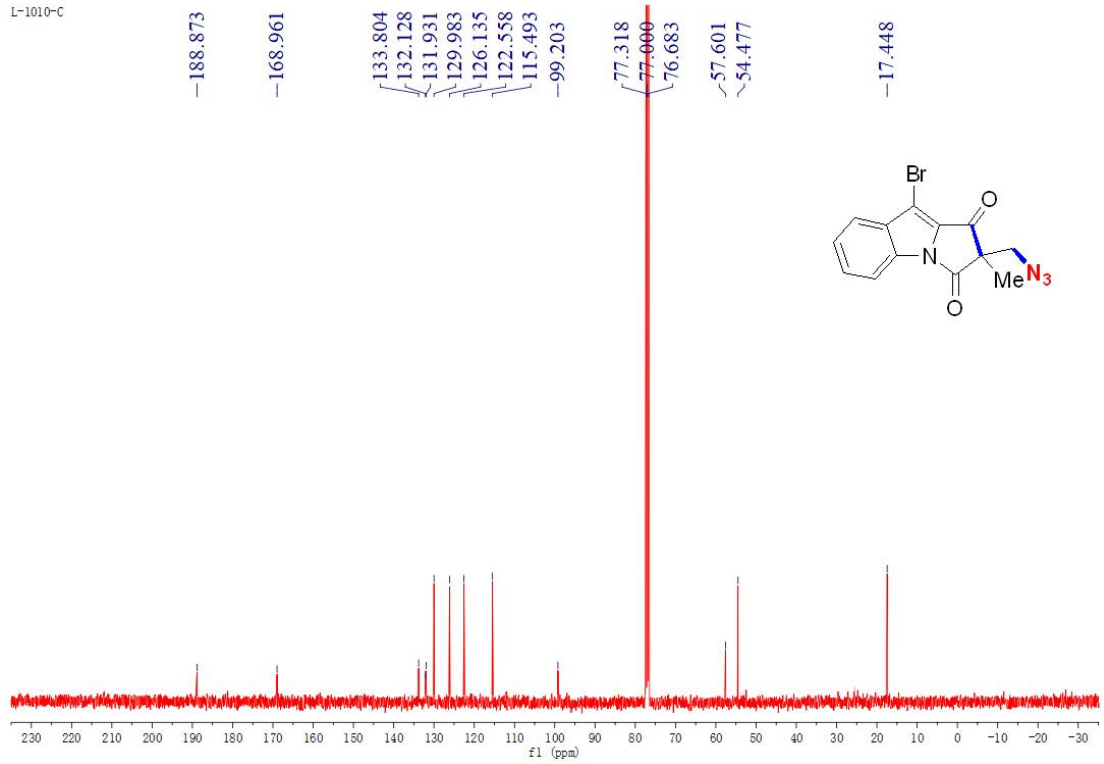
17-^{13}C NMR (150 MHz, $CDCl_3$)



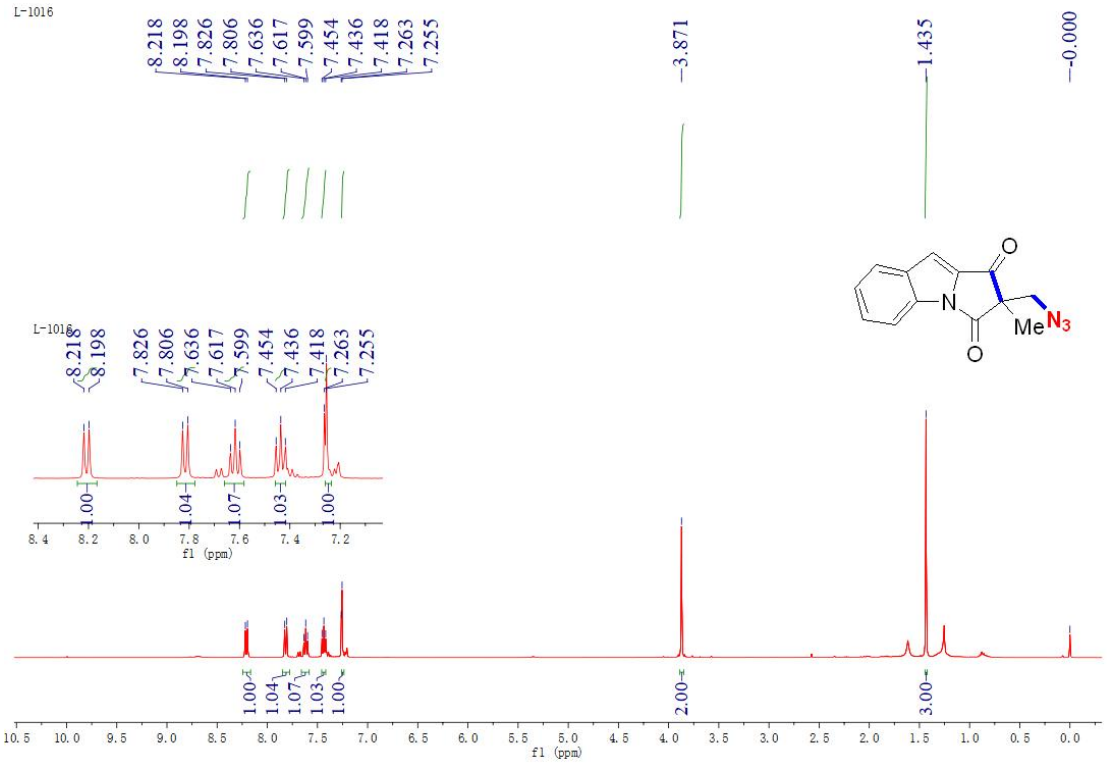
18-^{1}H NMR (400 MHz, $CDCl_3$)



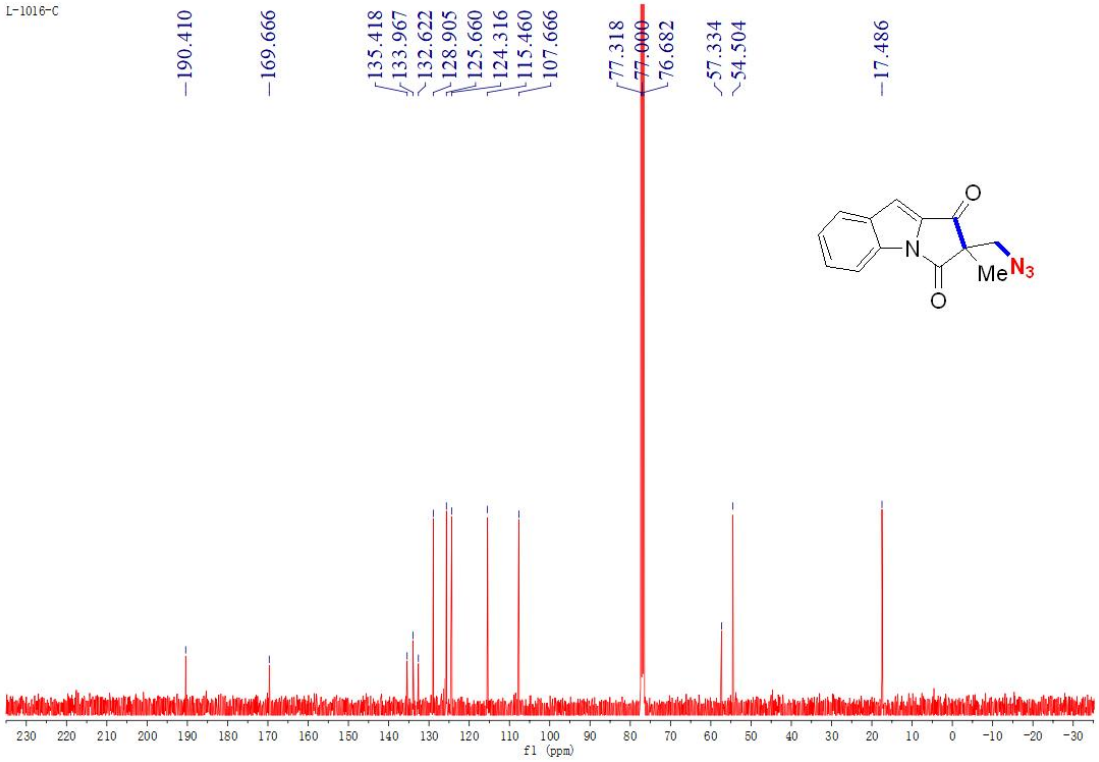
18-^{13}C NMR (100 MHz, $CDCl_3$)



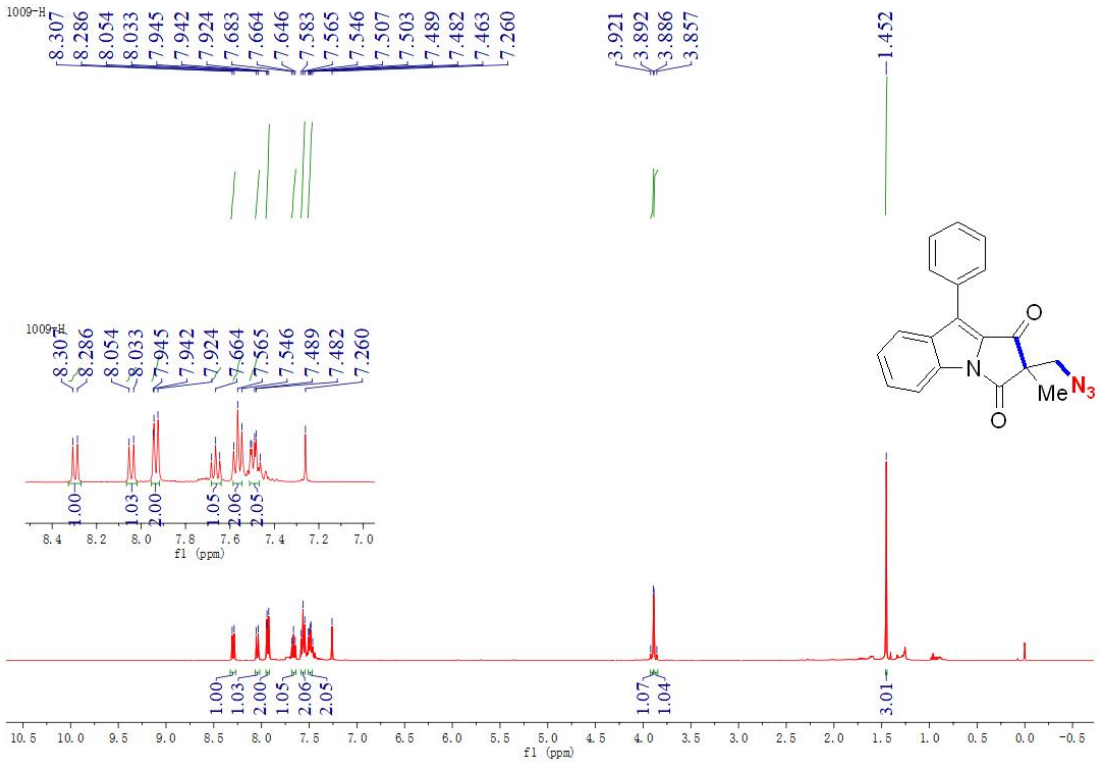
19-^{1}H NMR (400 MHz, $CDCl_3$)



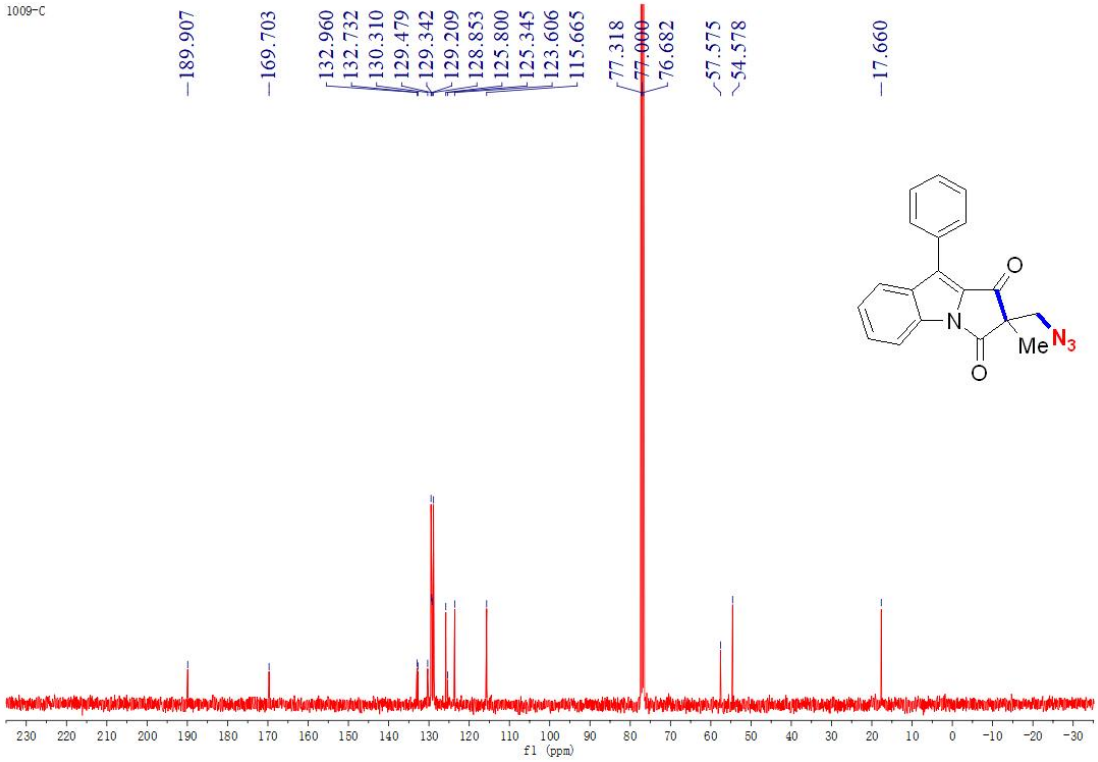
19-^{13}C NMR (100 MHz, $CDCl_3$)



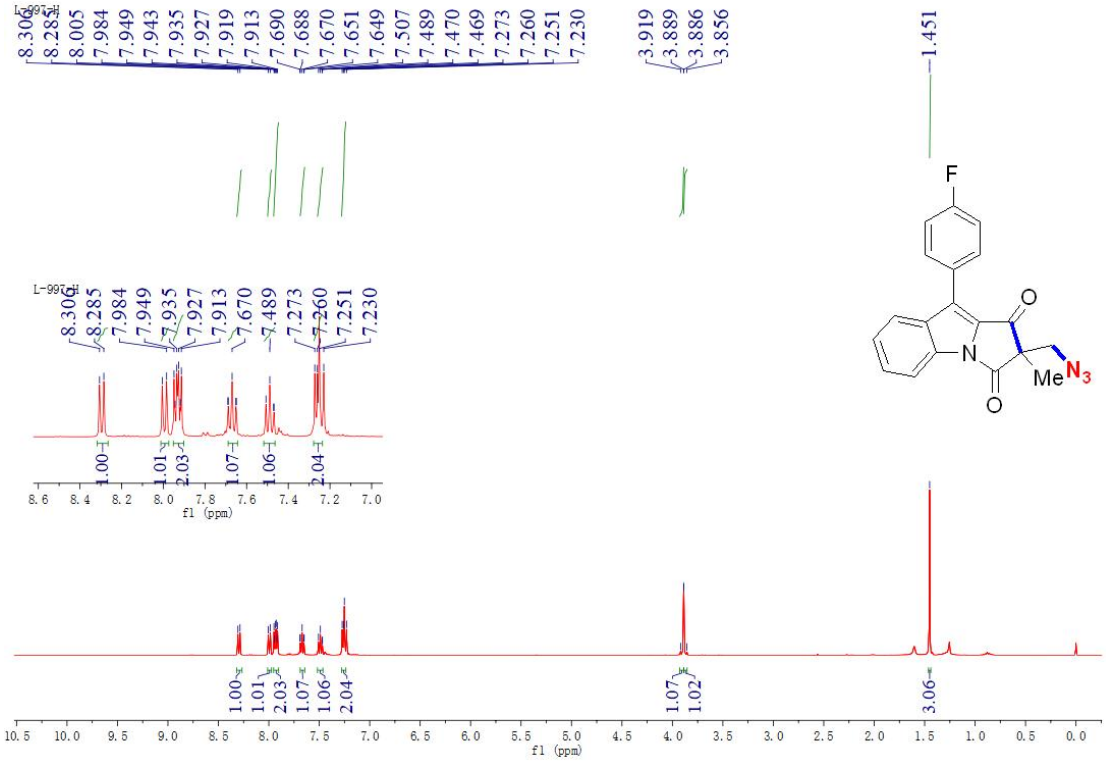
20-^{1}H NMR (400 MHz, $CDCl_3$)



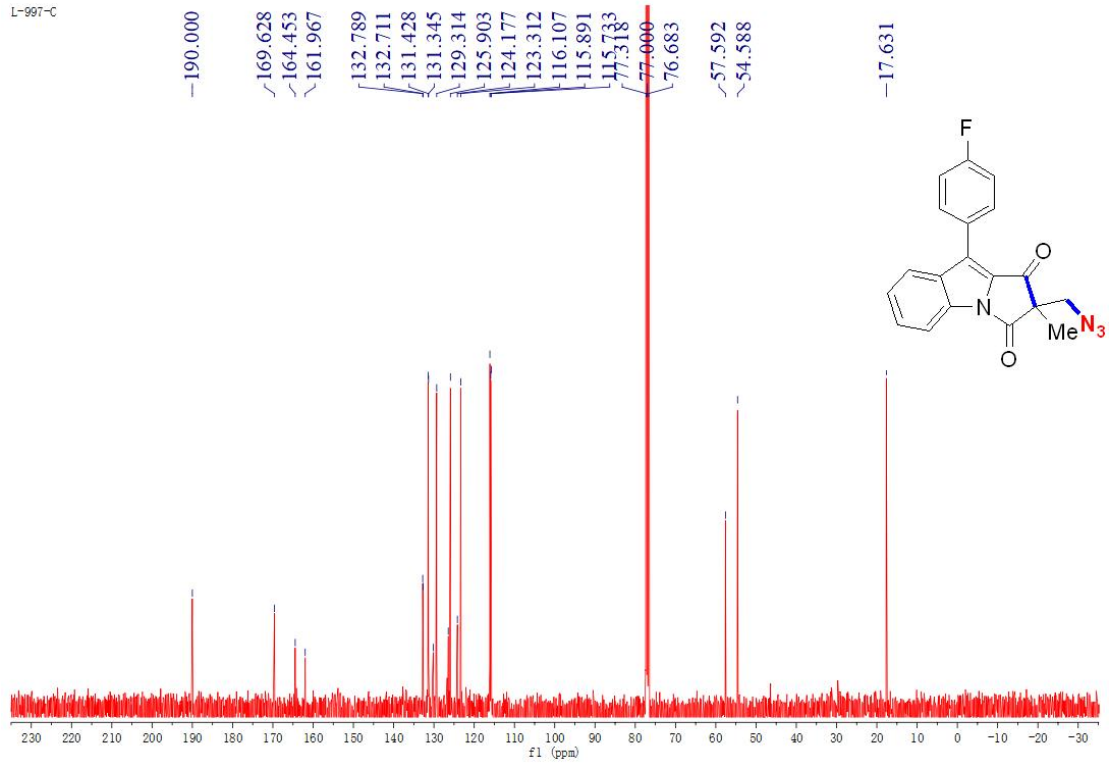
20-^{13}C NMR (100 MHz, $CDCl_3$)



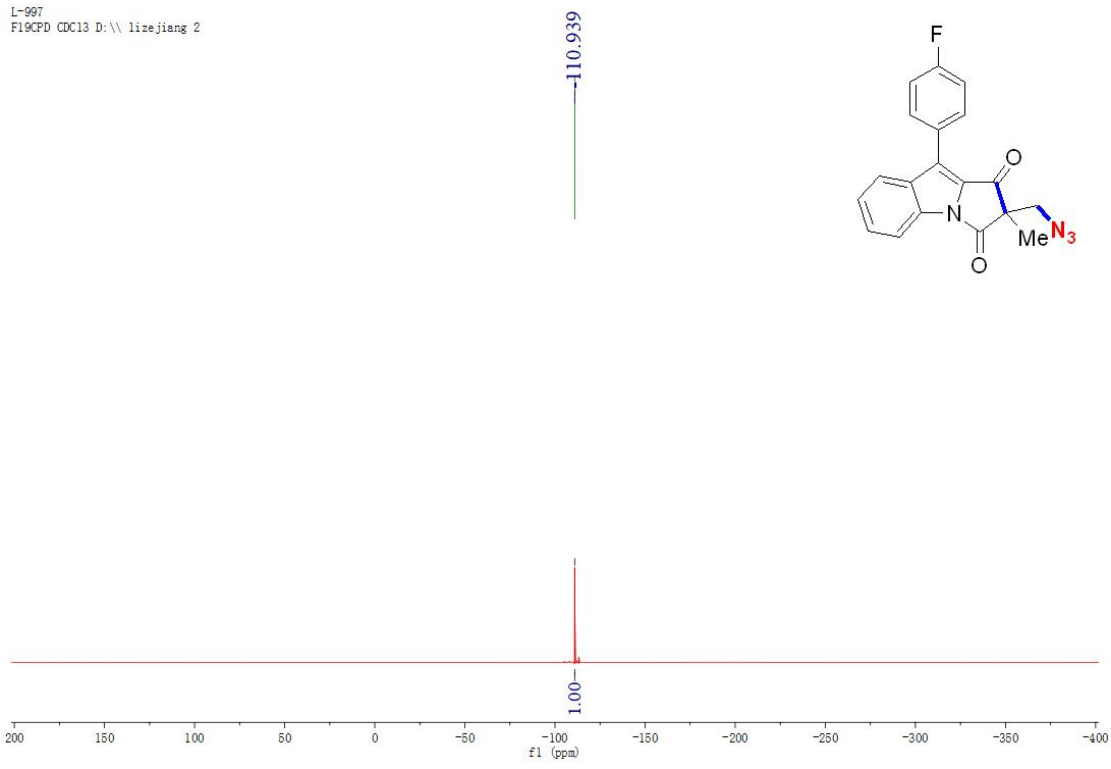
21-^{1}H NMR (400 MHz, $CDCl_3$)



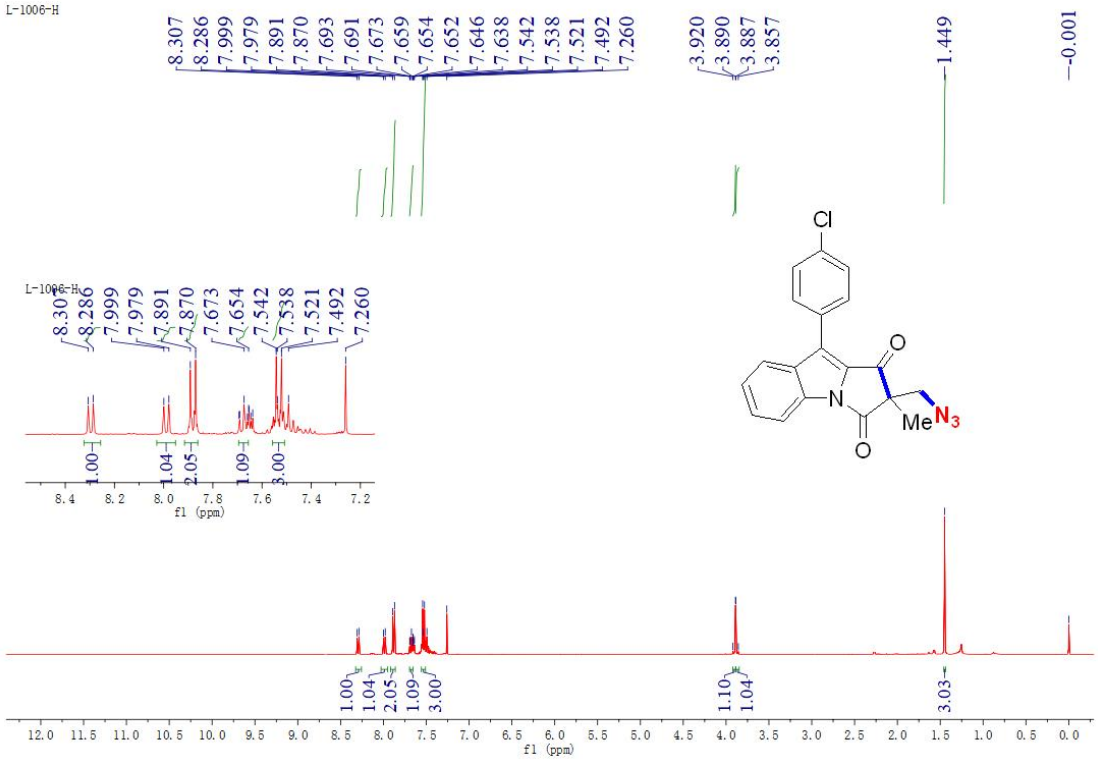
21-^{13}C NMR (100 MHz, $CDCl_3$)



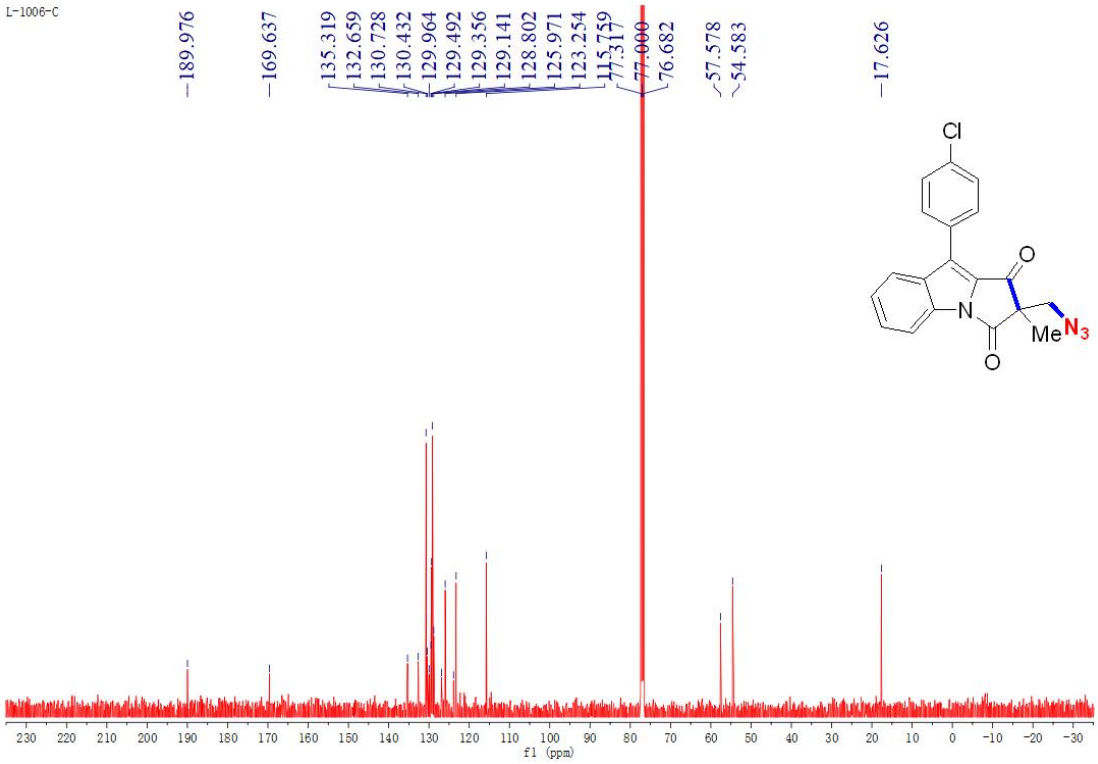
21-^{19}F NMR (565 MHz, $CDCl_3$)



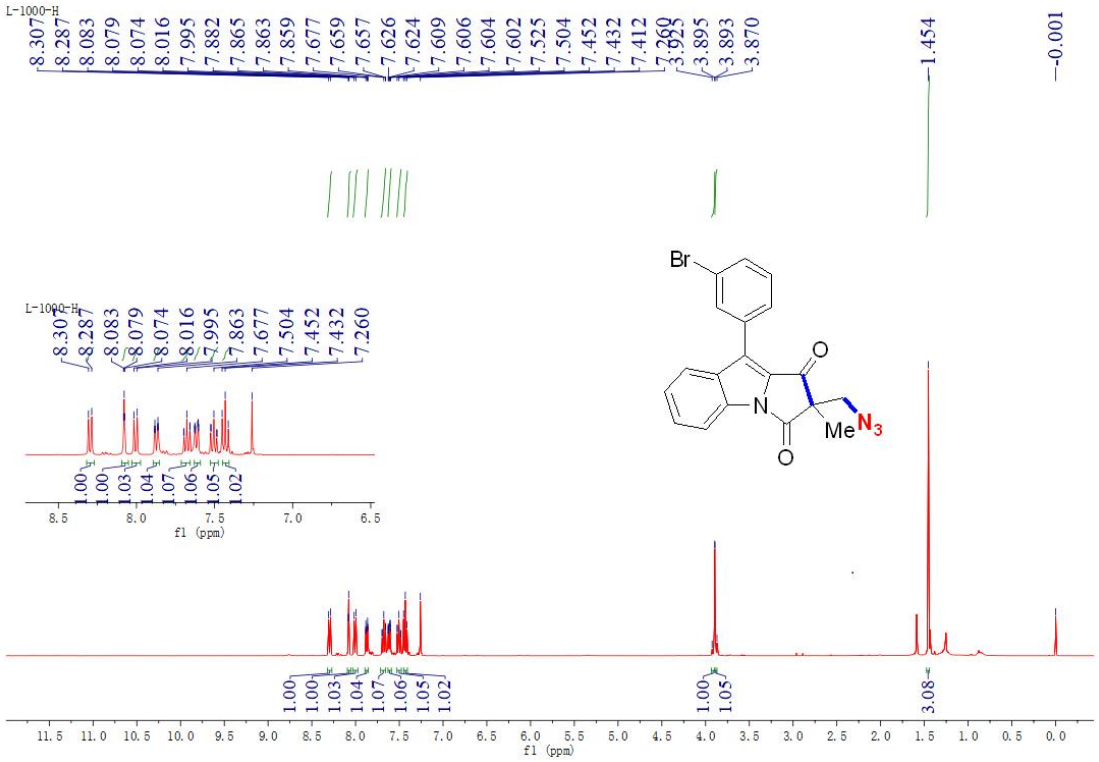
22-^{1}H NMR (400 MHz, $CDCl_3$)



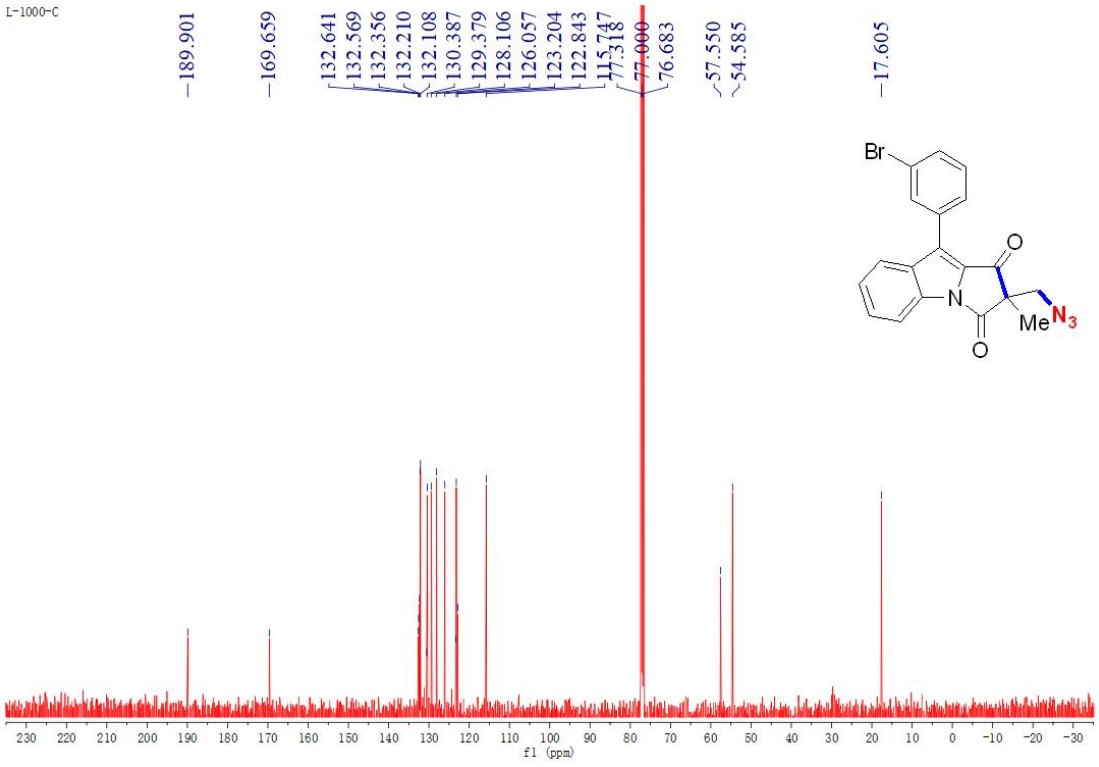
22-^{13}C NMR (100 MHz, $CDCl_3$)



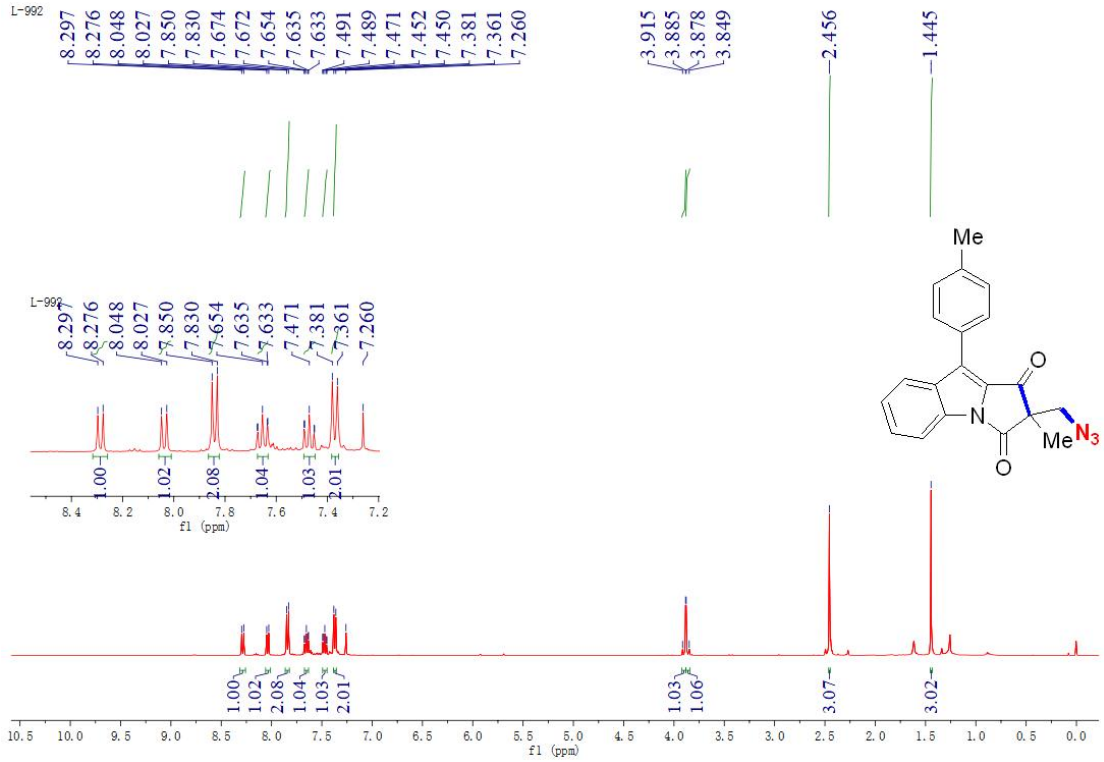
23-^{1}H NMR (400 MHz, $CDCl_3$)



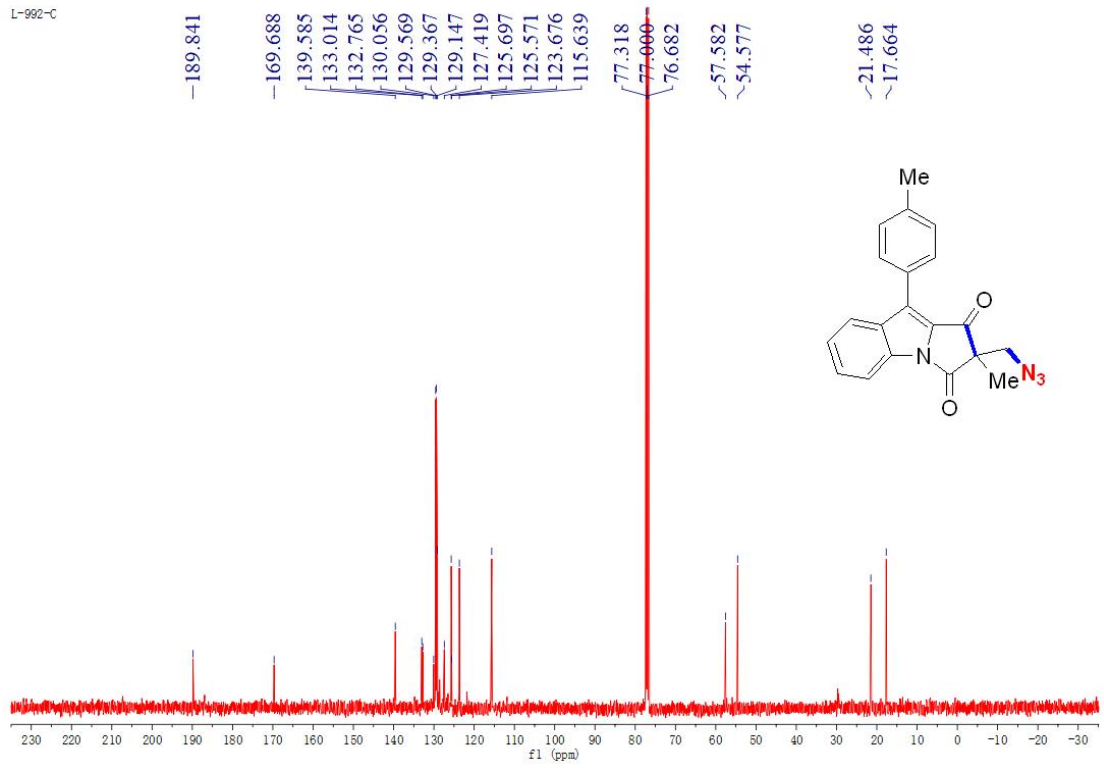
23-^{13}C NMR (100 MHz, $CDCl_3$)



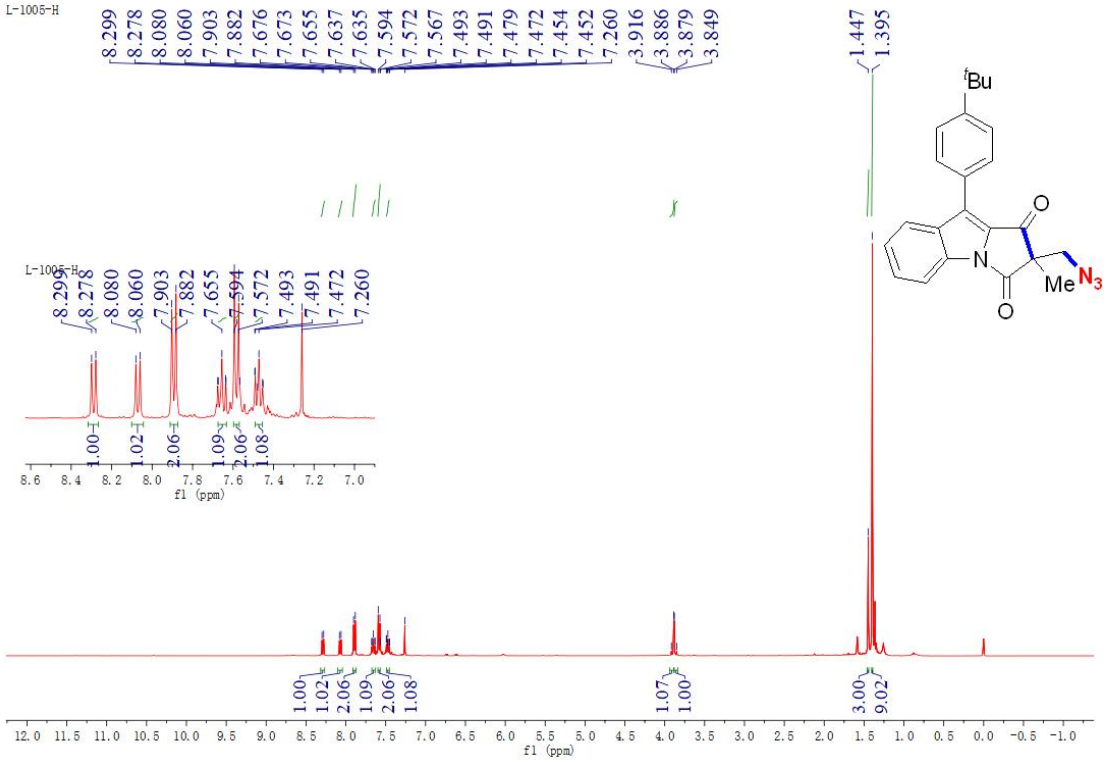
24-^{1}H NMR (400 MHz, $CDCl_3$)



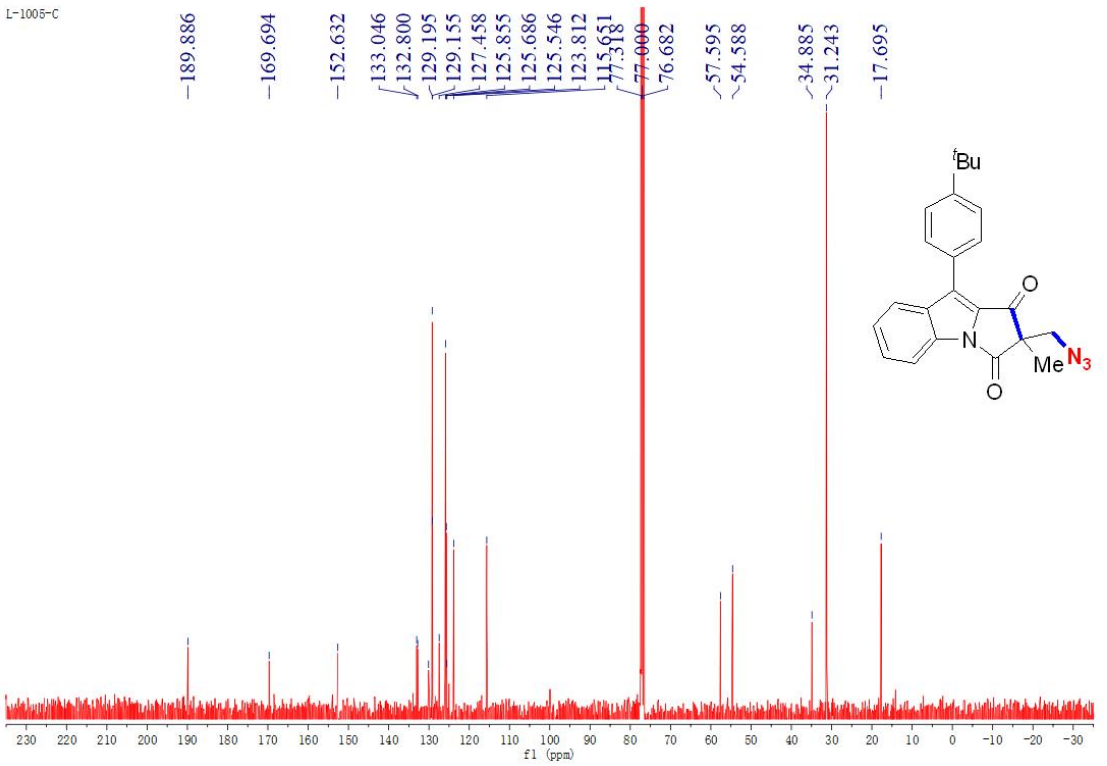
24-^{13}C NMR (100 MHz, $CDCl_3$)



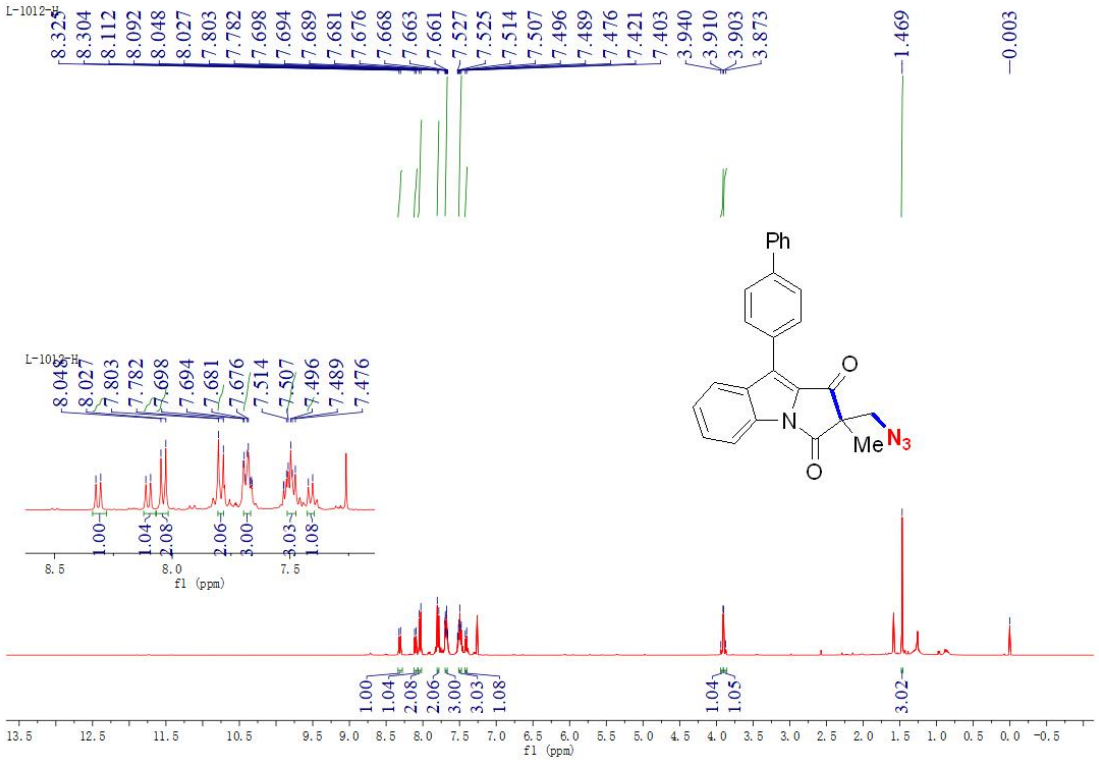
25-^{1}H NMR (400 MHz, $CDCl_3$)



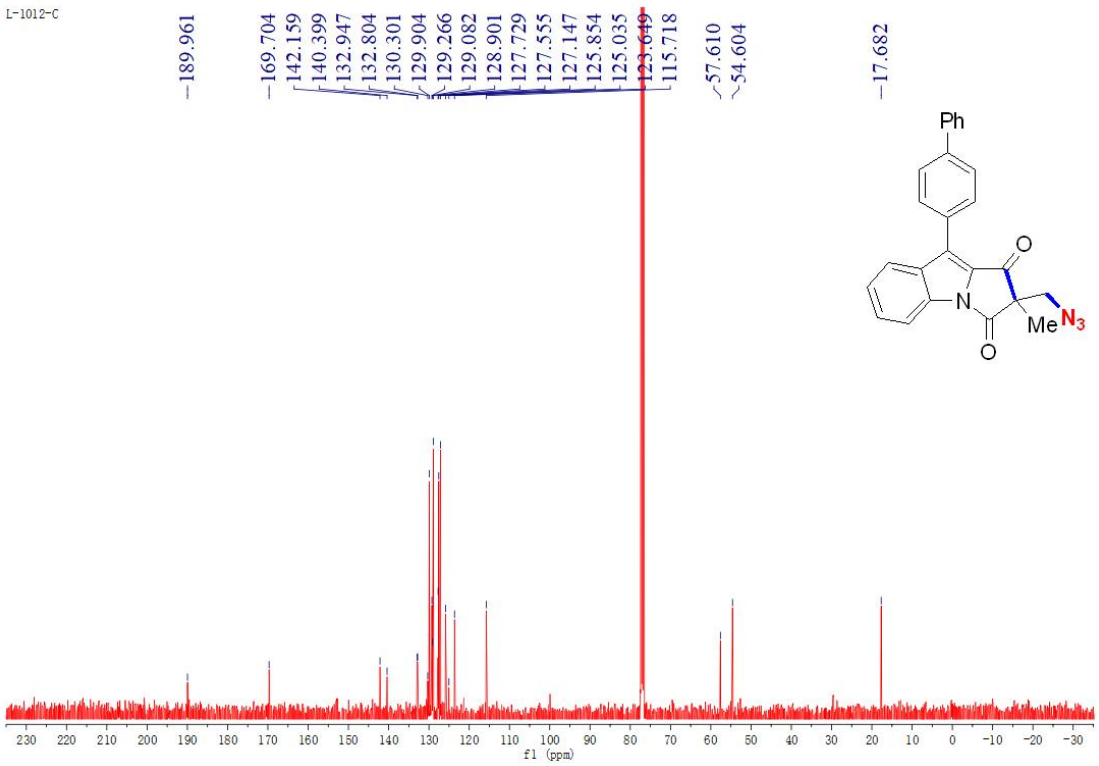
25-^{13}C NMR (100 MHz, $CDCl_3$)



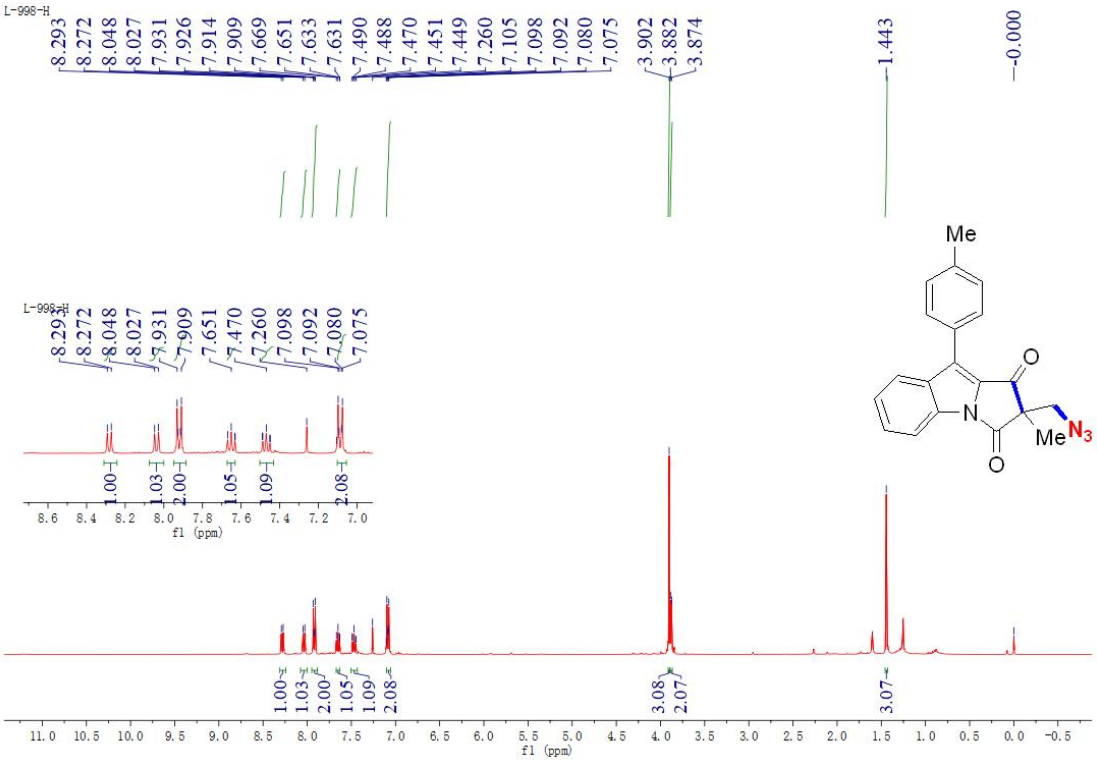
26-^{1}H NMR (400 MHz, $CDCl_3$)



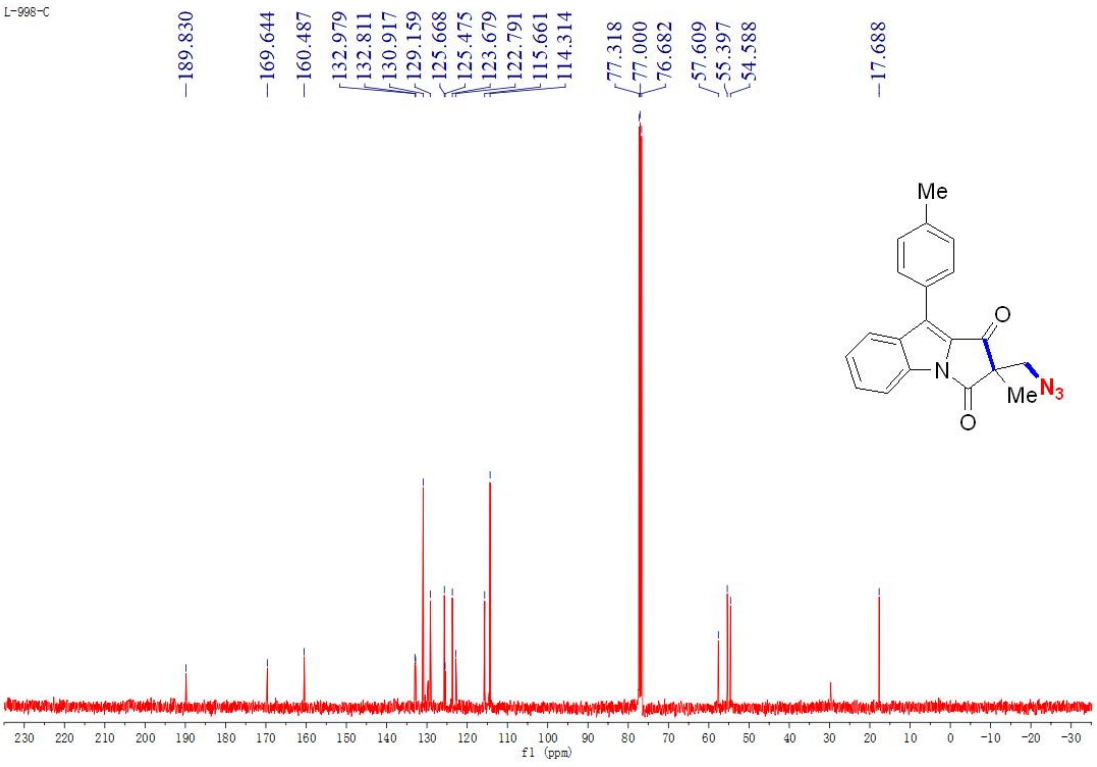
26-^{13}C NMR (100 MHz, $CDCl_3$)



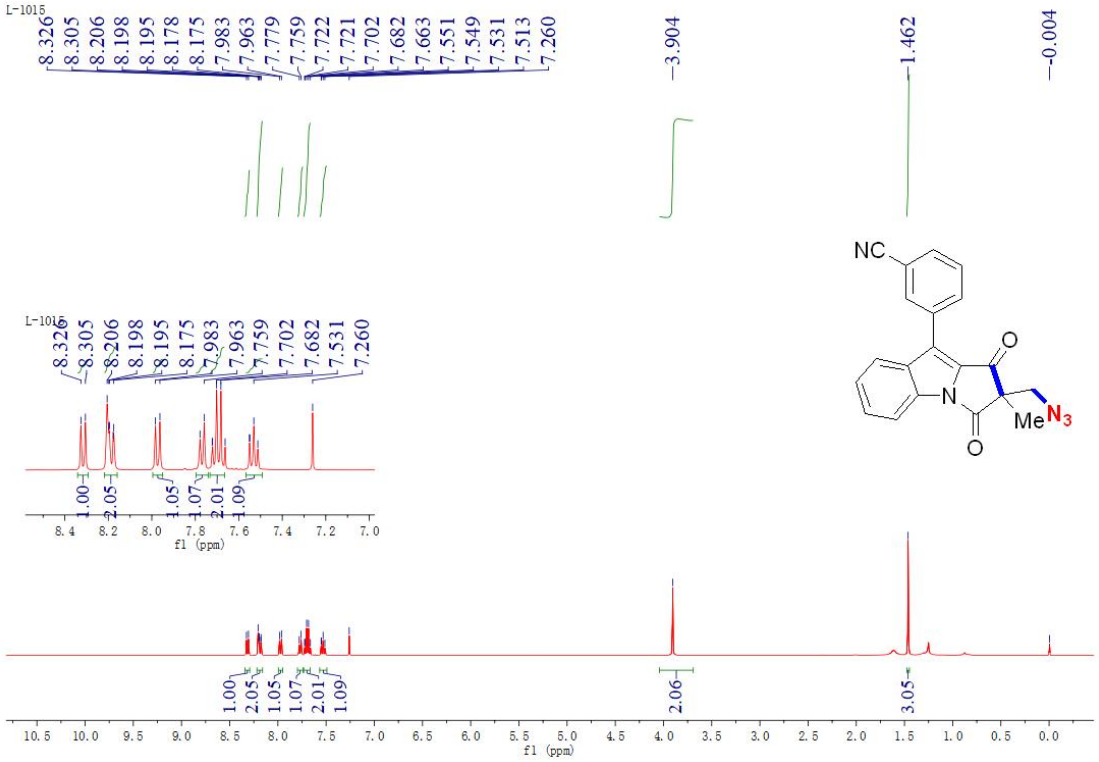
27-^{1}H NMR (400 MHz, $CDCl_3$)



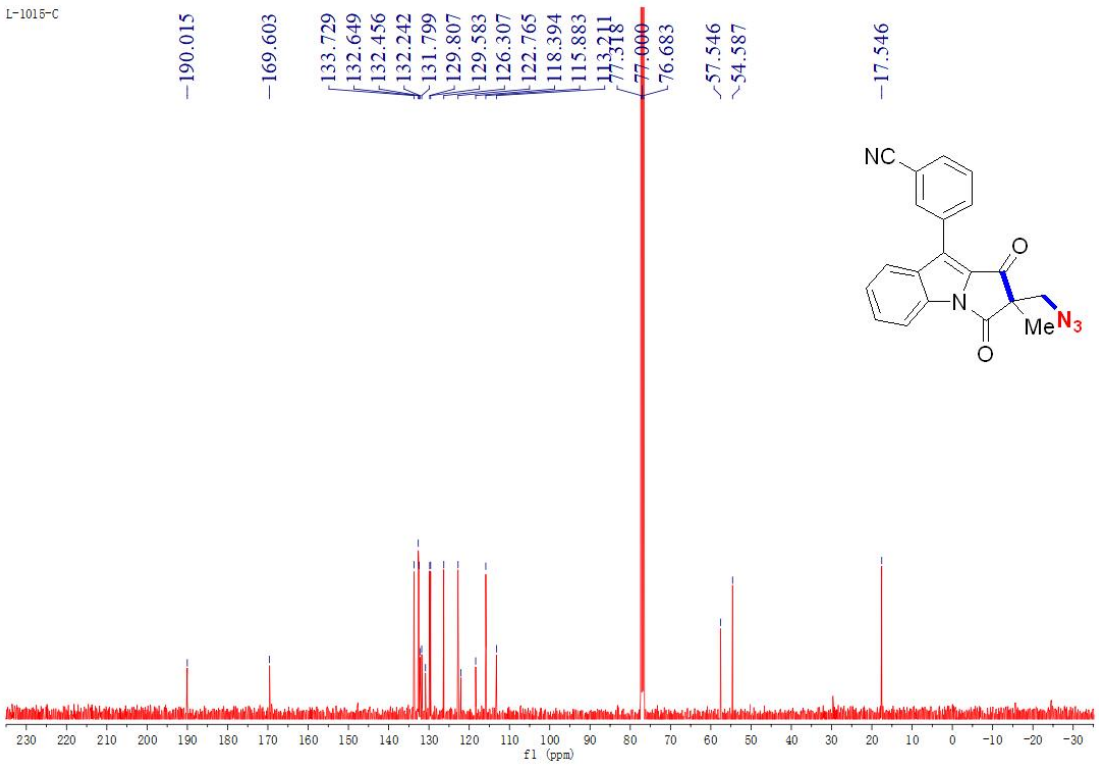
27-^{13}C NMR (100 MHz, $CDCl_3$)



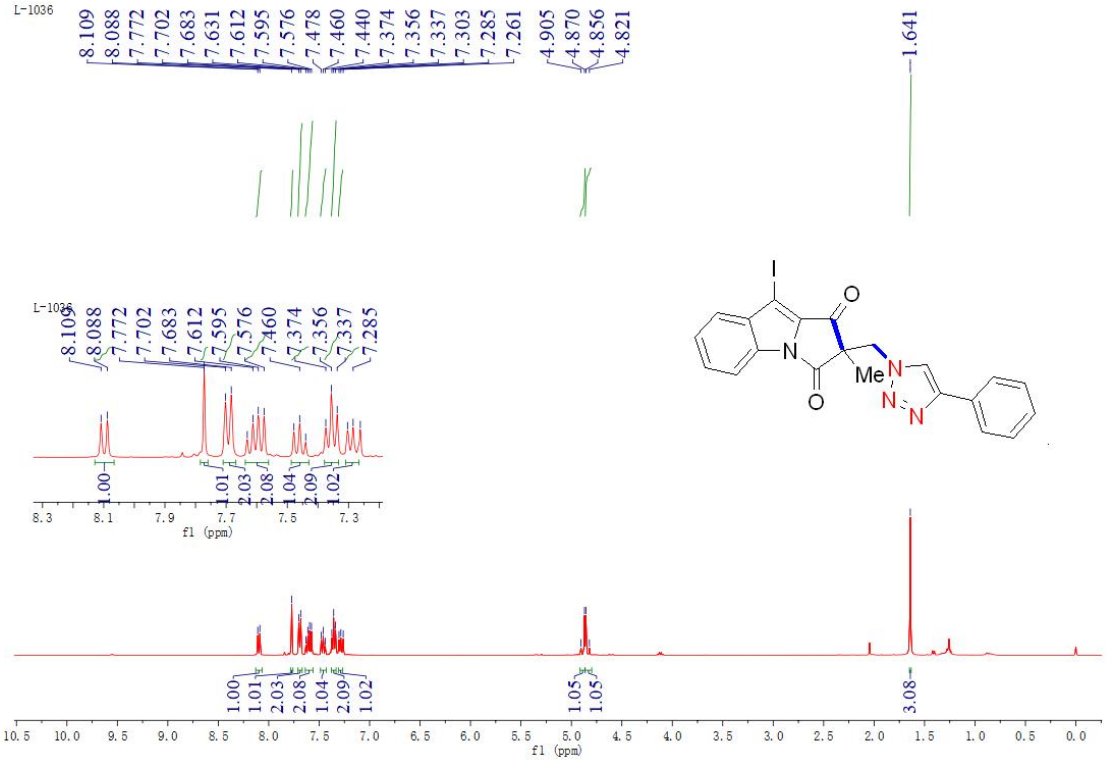
28-^{1}H NMR (400 MHz, $CDCl_3$)



28-^{13}C NMR (100 MHz, $CDCl_3$)



29-^{1}H NMR (400 MHz, $CDCl_3$)



29-^{13}C NMR (100 MHz, $CDCl_3$)